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VOLUME 8: CONTROL OF ACCIDENTAL RELEASES OF HYDROGEN FLUORIDE

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ABSTRACT

The accidental releases of a toxic chemical at Bhopal, India in 1984 was a milestone in creating an increased public awareness of toxic release problems. As a result of other, perhaps less dramatic incidents in the past, portions of the chemical industry were aware of this problem long before these events. These same portions of the industry have made advances in this area. Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community prompted the preparation of this manual and a planned series of companion manuals addressing accidental releases of toxic chemicals.

Anhydrous hydrogen fluoride has an IDLH (Immediately Dangerous to Life and Health) concentration of 20 ppm, which makes it a substantial acute toxic hazard.

Reducing the risk associated with an accidental release of hydrogen fluoride involves identifying some of the potential causes of accidental releases that apply to the process facilities that use hydrogen fluoride. In this manual, examples of potential causes are identified as are specific measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design practices, prevention, protection and mitigation technologies, and operation and maintenance practices. Conceptual cost estimates of example prevention, protection, and mitigation measures are provided.

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SECTION 1
INTRODUCTION

1.1 BACKGROUND

Increasing concern about the potentially disastrous consequences of accidental releases of toxic chemicals resulted from the Bhopal, India accident of December 3, 1984, which killed approximately 2,000 people and injured thousands more. A toxic cloud of methyl isocyanate was released. Concern about the safety of process facilities handling hazardous materials increased further after the accident at the Chernobyl nuclear power plant in the Soviet Union in April of 1986.

While headlines of these incidents have created the current awareness of toxic release problems, there have been other, perhaps less dramatic, incidents in the past. Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community prompted the preparation of this manual and a planned series of companion manuals addressing accidental releases of toxic chemicals.

Historically, major incidents in the United States involving hydrogen fluoride do not appear to have been common, although a release of uranium hexafluoride in Oklahoma in early 1986 decomposed to hydrogen fluoride resulting in at least one death and some injuries.

1.2 PURPOSE OF THIS MANUAL

The purpose of this manual is to provide technical information about hydrogen fluoride and specifically about prevention, protection, and mitigation measures for accidental releases of hydrogen fluoride. The manual addresses technological and procedural prevention, protection and mitigation measures associated with the storage, handling, and process operations involving hydrogen fluoride as it is used in the United States. This manual does not address uses of hydrogen fluoride not encountered in the United States.

This manual is intended as a summary for persons charged with reviewing and evaluating the potential for releases at facilities that use, store, handle, or manufacture hydrogen fluoride. It is not intended as a specification manual, and in fact refers the reader to additional technical manuals and other information sources for more complete information on the topics discussed. Other information sources include manufacturers and distributors of hydrogen fluoride, and technical literature on design, operation, and loss prevention in facilities handling toxic chemicals.

1.3 SOURCES AND USES OF HYDROGEN FLUORIDE

Hydrogen Fluoride (HF) is a significant commodity chemical, produced by sulfuric acid treatment of calcium fluoride in the natural mineral fluorspar. In 1985, approximately 180,000 tons of hydrogen fluoride were manufactured in the U.S. (1). Numerous references in the technical literature provide information on both the manufacture and uses of hydrogen fluoride. In the United States, the primary uses of hydrogen fluoride include:

- As a catalyst in petroleum refinery alkylation;
- Chlorofluorocarbon manufacture;
- Sodium aluminum fluoride manufacture;
- Uranium processing;
- Stainless steel pickling;

- Glass etching and polishing; and
- Repackaging.

Storage systems for hydrogen fluoride include small cylinders (e.g., 150-lb cylinder), bulk storage tanks, and railroad tank cars used for stationary storage.

In addition to anhydrous hydrogen fluoride (hydrogen fluoride gas), hydrofluoric acid, an aqueous solution of hydrogen fluoride, is also used. This manual focuses primarily on anhydrous hydrogen fluoride, but some considerations also apply to hydrofluoric acid.

1.4 ORGANIZATION OF THE MANUAL

Following this introductory section, the remainder of this manual presents technical information on specific hazards and categories of hazards for hydrogen fluoride and their control. As stated previously, these are examples only and are representative of only some of the hazards that may be related to accidental releases.

Section 2 discusses physical, chemical and toxicological properties of hydrogen fluoride. Section 3 describes the types of facilities which manufacture and use hydrogen fluoride in the United States. Section 4 discusses process hazards associates with these facilities. Hazard prevention and control are discussed in Section 5. Costs of example storage and process facilities reflecting different levels of control through alternative systems are also presented in Section 5. The examples are for illustration only and do not necessarily represent a satisfactory alternative control option in all cases. Section 6 presents a reference list. Appendix A presents the electromotive series of metals, Appendix B is a glossary of key technical terms that might not be familiar to all users of the manual, and Appendix C presents selected conversion factors between metric (SI) and English measurement units.

SECTION 2

CHEMICAL CHARACTERISTICS

This section of the report describes the physical, chemical, and toxicological properties of hydrogen fluoride as they relate to accidental release hazards.

2.1 PHYSICAL PROPERTIES

Anhydrous hydrogen fluoride is a clear, colorless, corrosive liquid with a pungent, irritating odor. With a boiling point of about 67°F, at room temperature and atmospheric pressure, it is a colorless, corrosive, toxic gas. Hydrogen fluoride is hygroscopic and fumes upon exposure to moist air. Hydrogen fluoride in aqueous solutions is hydrofluoric acid, a highly corrosive liquid. Concentrated aqueous solutions also boil at relatively low temperatures and fume upon contact with moist air. The physical properties of anhydrous and aqueous hydrofluoric acid are listed in Tables 2-1 and 2-2, respectively (2).

As a result of the relatively low boiling point of hydrogen fluoride, spills and leaks of liquid can result in hazardous releases to the atmosphere nearly as severe as direct gas or vapor releases. In addition, since the vapor density of hydrogen fluoride is greater than that of air, releases will remain close to the ground and could create a potentially dangerous situation for workers and surrounding communities.

Liquid hydrogen fluoride has a large coefficient of thermal expansion. As a result, liquid-full equipment is a special hazard. A liquid-full vessel is a vessel that is not vented and is filled with liquid hydrogen fluoride

TABLE 2-1. PHYSICAL PROPERTIES OF HYDROGEN FLUORIDE

		Reference
CAS Registry Number	07664-39-3	
Chemical Formula	HF	
Molecular Weight	20.01	
Normal Boiling Point	67.12 °F @ 14.7 psia	2
Melting Point	-118.4 °F	2
Liquid Specific Gravity (H_2O=1)	0.991 @ 67.15 °F	3
Vapor Specific Gravity (air=1)	2.4 @ 68 °F	4
Vapor Pressure	17.8 psia @ 77 °F	2
Vapor Pressure Equation		5

$$\log Pv = A - \frac{B}{T+C}$$

where: Pv = vapor pressure, mm Hg
T = temperature, °C
A = 7.68098, a constant
B = 1,475.60, a constant
C = 287.88, a constant

Liquid Viscosity	0.256 centipoises @ 32 °F	5
Solubility in Water	Complete	2
Specific Heat at Constant Volume (vapor)	0.55 Btu/(lb-°F) @ 68 °F	2

(Continued)

TABLE 2-1 (Continued)

		Reference
Specific Heat at Constant Pressure (vapor)	2.99 Btu/(lb-°F) @ 68 °F	2
Specific Heat at Constant Pressure (liquid)	0.62 Btu/(lb- F) @ 68 °F	2
Latent Heat of Vaporization	1.62 Btu/lb @ 67.15 °F	5
Liquid Surface Tension	10.1 dynes/cm @ 32 °F	2
Average Coefficient of Thermal Expansion, 0-60 °F	0.00112 °F	6

Additional properties useful in determining other properties from physical property correlations.

Critical Temperature	370 °F	2
Critical Pressure	940 psia	2
Critical Density	18.10 lb/ft^3	2
Energy of Molecular Interaction	355 K	7
Effective Molecular Diameter	3.240 Angstroms	7

with little or no vapor space present above the liquid. A liquid-full line is a section of pipe that is sealed off at both ends and is full of liquid hydrogen fluoride with little or no vapor space. In these situations, there is no room for thermal expansion of the liquid, and temperature increases can result in containment failure.

TABLE 2-2. PHYSICAL PROPERTIES OF 70% AQUEOUS HYDROFLUORIC ACID

		Reference
Boiling Point	152.06°F @ 14.7 psia	6
Freezing Point	-94.3°F	6
Vapor Pressure	1.1. psia @ 32°F	6
Specific Gravity (H_2O = 1)	1.258 @ 32-39.2°F	6
Specific Heat	0.75 Btu/lb-°F @ 64-68 °F	6

2.2 CHEMICAL PROPERTIES AND REACTIVITY

Hydrogen fluoride, whether anhydrous or in aqueous solutions, is a highly reactive chemical. The most significant chemical properties contributing to the potential for releases are as follows (2,8):

- Anhydrous hydrogen fluoride rapidly absorbs moisture to form highly corrosive hydrofluoric acid. Hydrofluoric acid is corrosive to most metals and results in the formation of hydrogen gas in the presence of moisture. This corrosiveness can lead to equipment failure, and the potential buildup of hydrogen gas in confined areas presents a fire and explosion hazard.

- Hydrogen fluoride reacts with metals listed above hydrogen in the Electromotive Series of Metals (a ranking of metals based on standard electrode potentials, see Appendix A, page 109) to form fluoride salts. In addition, it reacts with metal carbonates, oxides, and hydroxides. Accumulation of these fluoride compounds can render valves and other close-fitting moving parts inoperable in a process system, causing possible equipment or process failures. Such compounds also can contribute to the fouling of critical heat transfer surfaces in process operations. Hydrogen fluoride also attacks glass, silicate ceramics, leather, natural rubber, and wood, but does not promote their combustion.

- Considerable heat evolves when anhydrous hydrogen fluoride or concentrated hydrofluoric acid is diluted with water. Violent reactions can result from the inappropriate addition of water or caustic solutions to these materials.

- Anhydrous hydrogen fluoride and hydrofluoric acid react with silica (SiO_2) and SiO_2-containing substances to form silicon tetrafluoride (SiF_4) and fluorosilicic acid. SiF_4, a colorless gas at ambient temperatures, is highly toxic. An equilibrium mixture of SiF_4 in the presence of moisture also contains hydrogen fluoride and hydrofluoric acid.

- Anhydrous hydrogen fluoride and hydrofluoric acid react exothermally with organic and inorganic reducing agents, but do not promote their combustion.

- Anhydrous hydrogen fluoride reacts with cyanides and sulfides to produce toxic hydrogen cyanide and hydrogen sulfide, respectively. This can result in potentially explosive mixtures in confined areas since both hydrogen cyanide and hydrogen sulfide are flammable.

2.3 TOXICOLOGICAL AND HEALTH EFFECTS

Hydrogen fluoride is a highly toxic, and is a highly corrosive and severe irritant to the skin, eyes, and respiratory system. The toxicology of hydrogen fluoride has been studied through accidental human exposure and through animal studies (9,10,11,12,13). The acute effects of very short term exposure to elevated concentrations of hydrogen fluoride, however, are not well documented.

The concentrations at which various acute effects occur vary significantly with time of exposure and with individuals. For instance, inhalation of 50 parts per million (ppm) hydrogen fluoride for 30 to 60 minutes might be fatal, while a concentration of 110 ppm inhaled for 1 minute might be tolerated with only the initial onset of toxic effects. Less severe exposures cause irritation of the nose and eyes, smarting of the skin, and some degree of conjunctival and respiratory irritation. More severe exposures can lead to severe irritation of the eyes and eyelids, ulceration of the skin, inflammation and congestion of the lungs, and eventual cardiovascular collapse and death. Additional effects may include dyspnea, bronchopneumonia, cyanosis, shock, muscle spasms, convulsions, parasthesias, jaundice, oliguria, albuminuria, hematuria, nausea, vomiting, abdominal pain, diarrhea, and burns of the mouth, esophagus, and digestive tract. A concentration of 20 ppm has been designated as the IDLH (Immediately Dangerous to Life and Health), which is based on a 30 minute exposure. Table 2-3 presents a summary of some of the relevant exposure limits for hydrogen fluoride. Table 2-4 presents a summary of predicted human health effects of exposure to various concentrations of hydrogen fluoride.

TABLE 2-3. EXPOSURE LIMITS FOR HYDROGEN FLUORIDE

Exposure Limit	Concentration (ppm)	Description	Reference
IDLH	20	The concentration defined as posing an immediate danger to life and health (i.e. causes toxic effects for a 30-minute exposure).	14
PEL	3	A time-weighted 8-hour exposure to this concentration, as set by the Occupational Safety and Health Administration (OSHA), should result in no adverse effects for the average worker.	10
LC_{LO}	50	This concentration is the lowest published lethal concentration for a human over a 30- minute exposure.	10
TC_{LO}	110	This concentration is the lowest published concentration causing toxic effects (irritation) for a 1-minute exposure.	10

TABLE 2-4. PREDICTED HUMAN HEALTH EFFECTS OF EXPOSURE TO VARIOUS CONCENTRATIONS OF HYDROGEN FLUORIDE

ppm	Predicted Effect
0.5 - 3 ppm	Odor threshold
2 ppm	Repeated 6-hour exposures can result in stinging eyes and facial skin, and nasal irritation
>10 ppm	Possible lung injury
>50 ppm	Vapor is intolerably irritating and causes damage to the lungs; inhalation may result in serious injury

Source: Reference 11

SECTION 3
PROCESS FACILITY DESCRIPTIONS

This section provides brief descriptions of the manufacture and uses of hydrogen fluoride in the United States. Major hazards of these processes associated with accidental releases are discussed in Section 4. Preventive measures associates with these hazards are discussed in Section 5.

3.1 HYDROGEN FLUORIDE MANUFACTURE

Hydrogen fluoride is manufactured by the reaction of the fluorine containing mineral, fluorospar, with sulfuric acid. Figure 3-1 presents a block diagram of a typical hydrogen fluoride manufacturing process.

Finely ground acid grade fluorospar (greater than 97 percent CaF) is reacted in a heated rotating steel kiln with sulfuric acid to form calcium sulfate and hydrogen fluoride. The reaction is endothermic and heat is either supplied externally by direct fire to the rotary kiln or by the addition of sulfur trioxide and steam to the reaction zone (15,16). The heat absorbed is 603 Btu/lb (16).

In a typical process, fluorospar and sulfuric acid are fed continuously and concurrently to the kiln by a screw conveyor. The reaction is typically carried out at a temperature in the range of 392-482°F (15,16). In order to minimize energy consumption and corrosion of the reactor, the reaction is carried out at the lowest possible temperature resulting in good yields.

Crude product gas exits the reactor at approximately 212-338°F (15,16). It consists primarily of hydrogen fluoride saturated with sulfuric acid and a variety of impurities which vary depending on the composition of the raw materials used in the reaction. The gas is fed to a gas scrubber where it is

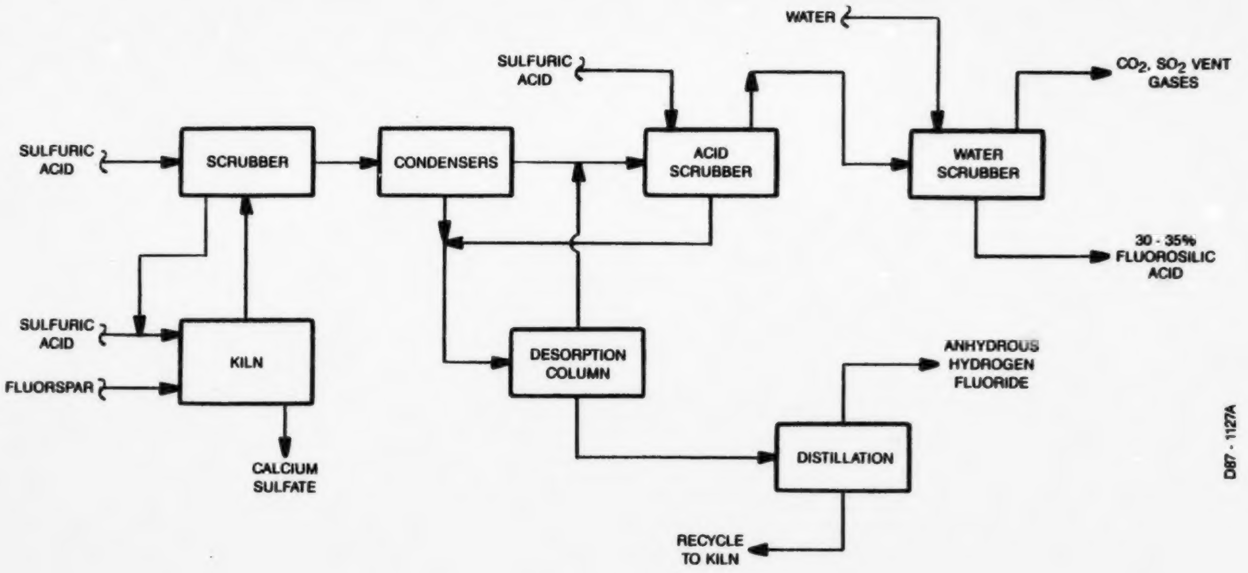
WATER
SULFURIC ACID
CO$_2$, SO$_2$ VENT GASES
SULFURIC ACID
SCRUBBER
CONDENSERS
ACID SCRUBBER
WATER SCRUBBER
30 - 35% FLUOROSILIC ACID
SULFURIC ACID
FLUORSPAR
KILN
DESORPTION COLUMN
ANHYDROUS HYDROGEN FLUORIDE
DISTILLATION
CALCIUM SULFATE
RECYCLE TO KILN
D87 - 1127A

Figure 3-1. Conceptual diagram of typical hydrogen fluoride manufacturing process.

scrubbed with sulfuric acid to remove small particles of fluorospar and/or calcium sulfate.

After leaving the gas scrubber, the crude hydrogen fluoride gas is cooled and liquified. In a typical process, the gas is cooled in shell and tube heat exchangers from 284-338°F to 41-104°F (15). The gas is then contacted with cold liquid hydrogen fluoride at -4 to -13°F in contact condensers to produce a liquid hydrogen fluoride product (15). The uncondensed gases are scrubbed with sulfuric acid to recover additional hydrogen fluoride. The final effluent gases are absorbed in water and recovered as fluorosilic acid.

Following liquefaction, the crude hydrogen fluoride is distilled to produce anhydrous hydrogen fluoride with a purity greater than 99.9 percent.

Since this process deals with the manufacture of hydrogen fluoride, hydrogen fluoride is present in high concentrations or relatively pure form in all areas following the reactor or kiln. Thus, the possibility of a large release of this chemical is greater than what might exist in a process where hydrogen fluoride is consumed as a reactant.

Specific high hazard areas in the manufacturing process, excluding bulk storage and transfer (discussed in Section 3.4), include the following:

- Reactor (kiln);
- Hydrogen fluoride scrubber;
- Hydrogen fluoride condensers;
- Desorption column; and
- Hydrogen fluoride distillation.

Although the reaction between sulfuric acid and calcium fluoride (fluorspar) is an endothermic reaction, the reactor or kiln can be considered a high hazard area since water may be present in the sulfuric acid used in the manufacturing process resulting in the formation of highly corrosive hydrofluoric acid. Additionally, the corrosiveness of hydrogen fluoride increases with temperature. Undetected corrosion could lead to equipment failure and a possible release of hydrogen fluoride.

In addition, other portions of the process, including the scrubbing units, could also be affected by similar corrosion problems as a result of hydrofluoric acid vapor being carried to other portions of the process. A properly designed system should use materials of construction which take this corrosion potential into account.

Shell and tube heat exchangers present a potential hazard from tube leakage where water is used as the cooling medium. Undetected small leaks over time could cause corrosion and eventually a failure. Also, a cooling system failure could result in overpressure and a resulting equipment failure.

An additional concern with cooling equipment in this process is the buildup of sulfur deposits on cooling surfaces resulting from sulfur and sulfur forming impurities present in the initial reaction products. These deposits can lead to clogging of piping and heat transfer equipment and loss of cooling efficiency.

The desorption and stripping unit operations are subject to potential overheating and overpressure since these operations have a thermal energy input. Loss of cooling in condensers could be a cause for overpressure. The reboilers and bottoms pumps are potential weak points in these systems since operating conditions are severe.

3.2 HYDROGEN FLUORIDE CONSUMPTION

The primary uses for hydrogen fluoride in the United States are chlorofluorocarbon manufacture, aluminum fluoride manufacture, sodium aluminum fluoride (cryolite) manufacture, petroleum alkylation, and uranium tetrafluoride manufacture. Additional uses are shown in Table 3-1. This subsection summarizes the major technical features, related to release hazards, of typical processing facilities found in the United States.

3.2.1 Hydrogen Fluoride Alkylation

A major use of hydrogen fluoride in the petroleum refining industry is for alkylation of olefinic hydrocarbons. In this process, anhydrous hydrogen fluoride is used as a liquid catalyst in the production of octane improvers for gasoline.

A block diagram of a typical hydrogen fluoride alkylation process is shown in Figure 3-2. This is one of several possible configurations for a hydrogen fluoride alkylation process. The processes differ primarily in the configuration of the reactor/settler section and whether or not they include a depropanizer unit (18).

Before entering the alkylation unit, the olefin-containing feed is treated to remove sulfur compounds and water. The feed is mixed with hydrofluoric acid and recycled isobutane, and the combined stream is fed to the reactor vessel. The alkylation reactor operates at a temperature in the range of 75-100°F and at a pressure of 80-115 pounds per square inch gage (psig) (18). Cooling water in a heat-exchange-tube bundle inside the alkylation reactor is commonly used in hydrogen fluoride alkylation to remove the heat generated by the exothermic reaction. The acid and organic phases of the reactor effluent separate in the settler, and the acid recycles to the reactor. A small portion of the acid is sent to a regenerator column where relatively pure hydrogen fluoride is distilled from a minor amount of heavy

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A major use of hydrogen fluoride in the petroleum refining industry is for alkylation of olefinic hydrocarbons. In this process, anhydrous hydrogen fluoride is used as a liquid catalyst in the production of octane improvers for gasoline.

A block diagram of a typical hydrogen fluoride alkylation process is shown in Figure 3-2. This is one of several possible configurations for a hydrogen fluoride alkylation process. The processes differ primarily in the configuration of the reactor/settler section and whether or not they include a depropanizer unit (18).

Before entering the alkylation unit, the olefin-containing feed is treated to remove sulfur compounds and water. The feed is mixed with hydrofluoric acid and recycled isobutane, and the combined stream is fed to the reactor vessel. The alkylation reactor operates at a temperature in the range of 75-100°F and at a pressure of 80-115 pounds per square inch gage (psig) (18). Cooling water in a heat-exchange-tube bundle inside the alkylation reactor is commonly used in hydrogen fluoride alkylation to remove the heat generated by the exothermic reaction. The acid and organic phases of the reactor effluent separate in the settler, and the acid recycles to the reactor. A small portion of the acid is sent to a regenerator column where relatively pure hydrogen fluoride is distilled from a minor amount of heavy

TABLE 3-1. TYPICAL USES OF HYDROGEN FLUORIDE

- Fluorocarbon manufacture
- Sodium aluminum fluoride (synthetic cryolite) manufacture
- Aluminum fluoride manufacture
- Gasoline alkylation catalyst
- Uranium tetrafluoride manufacture
- Stainless steel picking
- Manufacture of specialty metals
  e.g., columbium, tantalum, beryllium, and yttrium)
- Other chemical manufacture
  - ammonium bifluoride
  - ammonium fluoride
  - antimony pentafluoride
  - antimony trifluoride
  - barium fluroide
  - boron trifluoride
  - cadmium fluoride
  - cobaltous fluoride
  - cupric fluoride
  - difluorophosphoric acid
  - fluoboric acid
  - fluorine
  - fluasilicic acid
  - fluosulfonic acid
  - hexafluoroacetone
  - hexafluorophosphoric acid
  - lead tetrafluoride
  - lithium fluoride
  - magnesium fluoride
  - mercuric fluoride
  - monofluorophosphoric acid
  - perchlorofluoroacetone
  - potassium bifluoride
  - potassium fluoride
  - sodium bifluoride
  - sodium fluoride
  - stannous fluoride
  - tantalum fluoride
  - trifluoromethylnitrophenol
  - zinc fluoride

Source: Adapted from Reference 17.

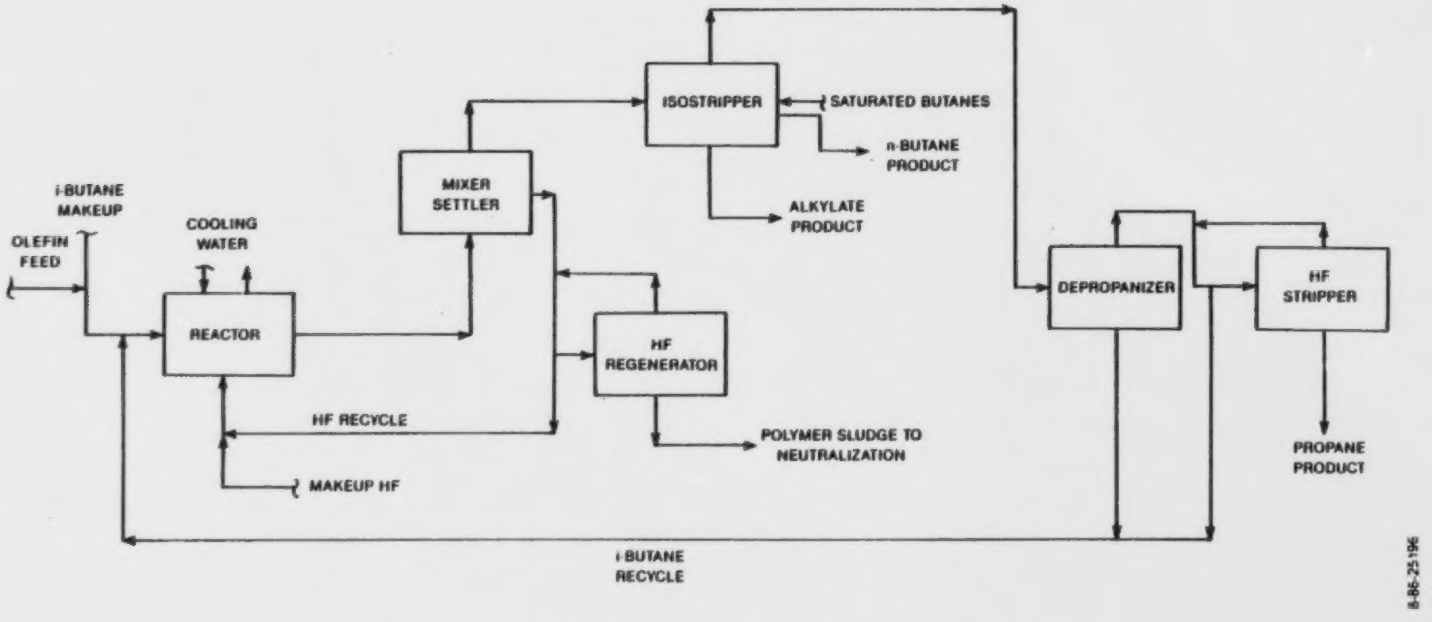
i-BUTANE MAKEUP
OLEFIN FEED
COOLING WATER
REACTOR
MIXER SETTLER
ISOSTRIPPER
SATURATED BUTANES
n-BUTANE PRODUCT
ALKYLATE PRODUCT
HF REGENERATOR
HF RECYCLE
MAKEUP HF
POLYMER SLUDGE TO NEUTRALIZATION
DEPROPANIZER
HF STRIPPER
PROPANE PRODUCT
i-BUTANE RECYCLE
8-86-25196

Figure 3-2. Conceptual diagram of typical hydrogen fluoride alkylation process.

organic compounds and water. The settler organic phase is fed to a fractionator, the isostripper, where isobutane and lighter components are separated. The bottoms product from the isostripper is motor alkylate. A portion of the isostripper overhead is depropanized with propane, containing some hydrogen fluoride, taken as an overhead stream. The propane is stripped of hydrogen fluoride and recovered as a bottoms stream.

From a hydrogen fluoride release perspective, a fundamental characteristic of the alkylation process is the use of hydrogen fluoride as a catalyst rather than a reactant. Only a small portion of the hydrogen fluoride catalyst is consumed in the alkylation process, approximately 0.002 - 0.007 lb/gal of product (28), and therefore the process has a number of critical areas where hydrogen fluoride is present in high concentrations or relatively pure form.

High hazard areas in the alkylation process, excluding bulk storage and transfer (discussed in Section 3.4), include the following:

- Feed treatment to remove water and sulfur compounds from the hydrocarbon feed;
- Reactor;
- Heat exchanger tube bundle within the reactor;
- Reactor cooling system;
- Hydrogen fluoride recycle circuits, including the settler;
- Hydrogen fluoride distillation, (the regenerator column); and
- Hydrogen fluoride stripping (from propane).

The feed treatment process to remove water and sulfur is a critical area of the process because these compounds promote corrosion. Water and hydrogen fluoride combine to form hydrofluoric acid which rapidly attacks many materials including carbon steel. A properly designed alkylation system should use materials of construction which take this corrosion potential into account and allow a certain feed moisture concentration to be maintained. Deficiencies or failures in the water removal system could lead to a protracted corrosion problem resulting eventually in equipment failure. Sulfur compounds also can lead to corrosion with results similar to those of water.

The reactor itself operates under mild conditions with near ambient temperatures. Since the reactor is a pressure vessel with an exothermic reaction, the potential exists for a runaway reaction resulting in overheating and overpressure. The normal elevated operating pressure, combined with the adverse effects of corrosion, could cause an equipment failure even under normal operating conditions. Proper system design must anticipate these hazards and incorporate appropriate safeguards. These safeguards should include highly reliable reactant feed control, pressure relief, and reactor cooling system controls and backup.

The presence of a heat exchange tube bundle within the reactor presents a potential hazard from tube leakage since water is used as the cooling medium. Small leaks over time could cause corrosion and eventually a failure. Also, since the reactor operates at pressures above typical cooling water circuit pressures, undetected leakage of acid into the cooling system could contribute to protracted corrosion and ultimately a cooling system failure. A cooling system failure could lead to a runaway reaction.

Hydrogen fluoride recycle circuits are subject to corrosion, with general vessel, piping, valve, or pump failures. Because the hydrogen fluoride is recycled, traces of moisture may enter the system and concentrate in the recycle stream, thus contributing to corrosion.

The hydrogen fluoride distillation and stripping unit operations are subject to potential overheating and overpressure since these operations have a thermal energy input. Loss of cooling in condensers could be a cause for overpressure. The reboilers and bottoms pumps are potential weak points in these systems since operating conditions are severe.

Since the alkylation process uses and produces highly flammable materials, other potential hazards associated with the entire process are fire and explosion. A fire or explosion is clearly a possible cause for release. An additional consideration is that hydrogen is formed as a corrosion product in the alkylation process. Rapid corrosion in any part of the system also carries with it an ignition potential as a result of possible hydrogen gas buildup.

3.2.2 Manufacture of Chlorofluorocarbons

A second principal use of hydrogen fluoride in the United States is in the manufacture of chlorofluorocarbons. One commercially important method of production is the successive replacement of chlorine in chlorinated hydrocarbon feedstocks (chlorocarbons) using hydrogen fluoride as a source of fluorine. A block diagram of a typical liquid phase chlorofluorocarbon manufacturing process is presented in Figure 3-3.

The liquid-phase reaction system for the manufacture of chlorofluorocarbons consists of a heated reaction vessel containing catalyst dissolved in a mixture of chlorocarbon, and partially fluorinated intermediates recycled to the reactor from downstream processing. Antimony pentafluoride or a mixture of antimony trifluoride and chlorine is typically used as catalyst. Liquid hydrogen fluoride and chlorocarbon are fed to the reactor. The reactor typically operates at a temperature and pressure of approximately 176°F and 100 psig, respectively (18). Although the fluorination reactions are exothermic, additional heat is added to the reactor because the reactor also serves as a reboiler for an enriching column. Crude product vapors evolved

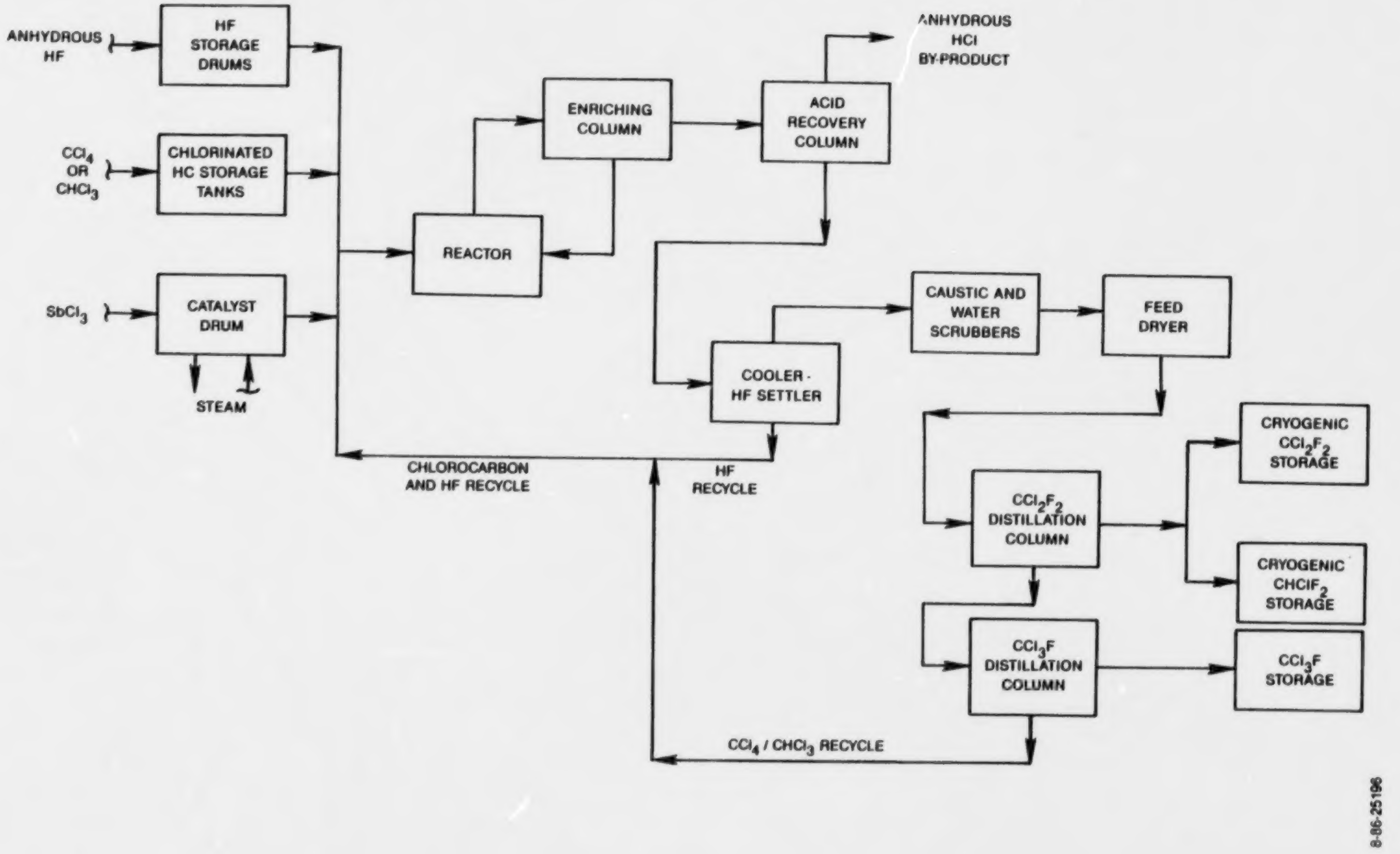
ANHYDROUS HF
HF STORAGE DRUMS
CCl_4 OR $CHCl_3$
CHLORINATED HC STORAGE TANKS
$SbCl_3$
CATALYST DRUM
STEAM
REACTOR
ENRICHING COLUMN
ACID RECOVERY COLUMN
ANHYDROUS HCl BY-PRODUCT
COOLER - HF SETTLER
CHLOROCARBON AND HF RECYCLE
HF RECYCLE
CAUSTIC AND WATER SCRUBBERS
FEED DRYER
CCl_2F_2 DISTILLATION COLUMN
CCl_3F DISTILLATION COLUMN
CRYOGENIC CCl_2F_2 STORAGE
CRYOGENIC $CHClF_2$ STORAGE
CCl_3F STORAGE
CCl_4 / $CHCl_3$ RECYCLE
8-86-25196

Figure 3-3. Conceptual diagram of typical fluorochlorocarbon process.

from the reactors are fed directly to the enriching column. The column is positioned so that the liquid bottoms flow by gravity as recycle to the reactor.

After being withdrawn from the enriching column, a stream containing hydrogen chloride, hydrogen fluoride, and the chlorofluorocarbon products is sent to an acid recovery column. This column typically operates at approximately 100 psig (18). Hydrogen chloride is concentrated at the top of the column and is recovered as a by-product. The bottoms contain the product fluorocarbons and residual hydrogen fluoride at a temperature of approximately 122°F (18). The hydrogen fluoride is removed in a hydrogen fluoride settler and is recycled to the reactor system. The mutual solubility of hydrogen fluoride and the fluorocarbons is temperature dependent and temperatures as low as -22°F are often required (18).

Trace impurities are removed from the fluorocarbon products by scrubbing with water and a dilute caustic solution. Following the scrubbing operations, the product stream is dried and fractionated into various chlorofluorocarbon products.

High hazard areas in the chlorocarbon manufacturing process, excluding bulk storage and transfer (discussed in Section 3.4), include the following:

- Feed treatment to remove water from the chlorocarbon feed streams;
- Reactor;
- Enriching and acid recovery columns;
- Hydrogen fluoride recovery unit; and
- Hydrogen fluoride recycle system.

Concerns for moisture removal in the feed treatment process are the same as those associated with alkylation feed treatment (Section 3.2.1).

An exothermic reaction occurs in the chlorofluorocarbon process, but since the reactor also serves as a reboiler to an enriching column, a reactor cooling system is not required for heat removal. In fact, additional heat is added. A potential hazard is overheating and overpressure caused by a malfunction in the temperature control system. Overheating and overpressure could also be caused by a loss of cooling in the enriching column condenser. Similar considerations apply to the other columns.

The hydrogen fluoride recycle system presents the hazards of vessel, piping, valve, and pump failure from potential corrosion caused by a buildup of trace quantities of water in the system.

3.2.3 Aluminum Fluoride Manufacture

Aluminum fluoride, specifically aluminum trifluoride, is manufactured using either a "wet", aqueous hydrofluoric acid process or a "dry," anhydrous hydrogen fluoride process.

In a typical "dry" process, alumina trihydrate is fed into the top zone of a fluidized bed reactor. Hydrogen fluoride gas enters the bottom zone of the reactor and receives heat from the aluminum trifluoride leaving the bottom of the reactor. The reaction is typically carried out at a temperature of approximately 1,100°F (2,19). Hydrogen fluoride and steam produced in the reaction are used to fluidize the bed. The effluent gas leaving the top of the reactor contains water vent, hydrogen fluoride, silicon tetrafluoride, dust, and other noncondensibles. These gases are typically used in the production of synthetic cryolite or are sent to a scrubber where they are removed by contacting them with water to form fluorosilicic acid (2,19).

The hazards associated with this process are the same as those presented previously in this manual for exothermic reactors, namely overtemperature and overpressure. In addition, this process also incorporates the potential for equipment failure resulting from undetected corrosion since hydrogen fluoride is extremely corrosive at the elevated temperatures found in this process.

3.2.4 Sodium Aluminum Fluoride (Cryolite) Manufacture

Synthetic cryolite (sodium aluminum fluoride) is manufactured by several methods. Several of these are methods are based on the use of fluorine-containing acids (e.g., hydrofluoric acid). However, processes based on the use of anhydrous hydrogen fluoride also exist.

In one such process, similar to that presented previously for aluminum trifluoride, sodium carbonate and alumina are fed to the top of a fluidized bed reactor (20). The reactor effluent gases are typically sent to a water scrubber for removal of hydrogen fluoride and formation and recovery of fluorosilicic acid. The solid product leaving the bottom of the reactor is compressed into capsules, heated in an oven at temperatures ranging from 1,290-1,210°F for several hours, and the final product, synthetic cryolite, is obtained (20).

The hazards associated with this process are similar to those presented for aluminum fluoride manufacture in the preceding subsection of this manual.

3.2.5 Uranium Tetrafluoride Manufacture

Uranium tetrafluoride is typically manufactured by the hydrofluorination of uranium dioxide with excess hydrogen fluoride. Figure 3-4 presents a flow diagram of a typical manufacturing process for uranium tetrafluoride.

In the manufacturing process several types of reactors are used including: stirred bed, vibrating tray, fluidized bed, and moving bed types.

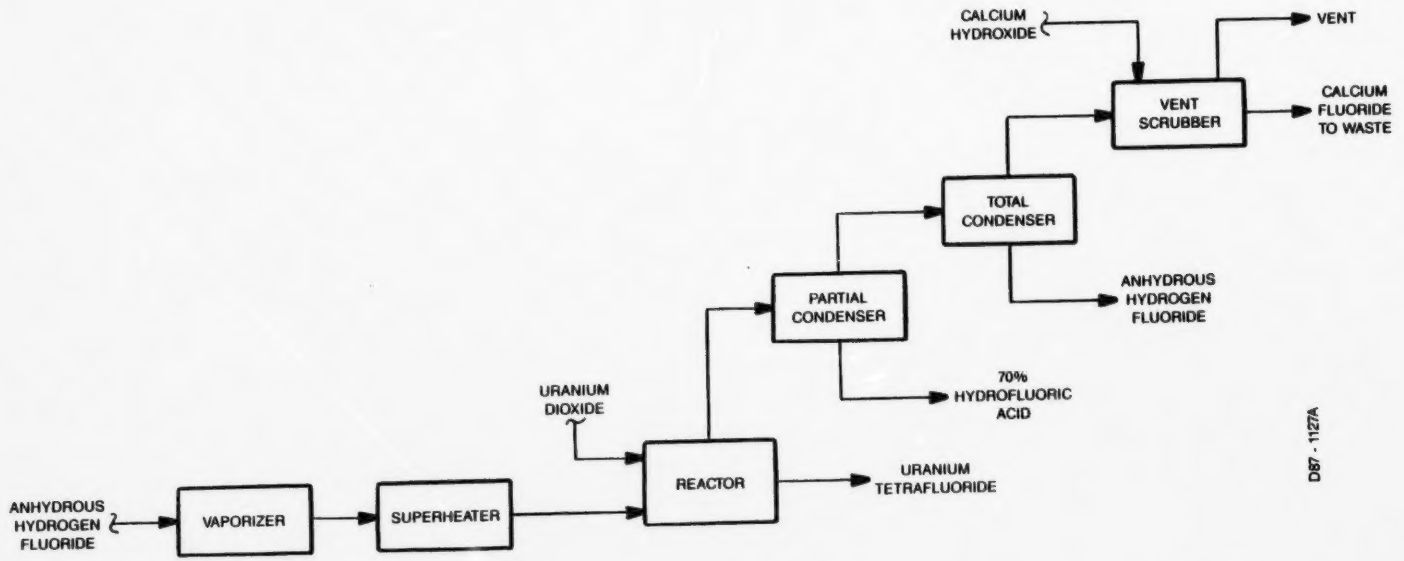
CALCIUM HYDROXIDE
VENT
VENT SCRUBBER
CALCIUM FLUORIDE TO WASTE
TOTAL CONDENSER
ANHYDROUS HYDROGEN FLUORIDE
PARTIAL CONDENSER
70% HYDROFLUORIC ACID
URANIUM DIOXIDE
REACTOR
URANIUM TETRAFLUORIDE
ANHYDROUS HYDROGEN FLUORIDE
VAPORIZER
SUPERHEATER
D87 - 1127A

Figure 3-4. Conceptual diagram of typical uranium tetrafluoride manufacturing process.

Whichever reactor is used, uranium dioxide is fed from storage hoppers by screw conveyors to the top of a the first reactor, in a series of reactors. Hydrogen fluoride is fed to the last reactor at approximately 200°F, after first passing through a vaporizer and a superheater (21). The series of reactors operate at an average temperature of approximately 1,000°F. Although the reaction is exothermic (43.2 kcal/mole), multi-zone electrical heating is used to maintain the required reactor temperature (21). Additionally, the reactor operates at a low pressure of about 2 psig since the seal hoppers and packing glands fail to function properl at higher pressures (21).

The uranium tetrafluoride product leaves through the bottom reactor and is collected in a small seal hopper. The effluent from the top reactor consists of hydrogen fluoride, water, and a small amount of non-condensible gas (21). It passes through a series of carbon filters used to collect any residual dust particles from the uranium dioxide charge. The effluent gas is then condensed in a series of water cooled shell and tube partial condensers which are maintained at approximately 140°F (21). The condensed liquid is approximately 70 percent hydrofluoric acid and is sent to storage. The resulting gases are condensed further using a shell and tube condenser operating at about -15°F (21). The condensed liquid is sent to anhydrous hydrogen fluoride storage. A lime slurry scrubber is used to remove any residual hydrogen fluoride from the vent gases before being released to the atmosphere.

High hazard areas in the uranium tetrafluoride manufacturing process, excluding bulk storage and transfer (discussed in Section 3.4), include the following:

- Reactor;
- Hydrogen fluoride vaporizing and preheating units; and
- Hydrogen fluoride condensers.

An exothermic reaction occurs in this process, but since additional heat is added to the systems to maintain a certain reaction temperature, a reactor cooling system is not required for heat removal. A potential hazard is overheating and overpressure caused by a malfunction in the temperature control systems. In the reactor section of this process, hydrogen fluoride is present at high temperatures and is very corrosive. Additionally, corrosive hydrofluoric acid is present in portions of the process. A properly designed system should use materials of construction which take this corrosion potential into account. Additionally, a level control system should be used in the uranium dioxide feed hopper to prevent it from being completely emptied. If such were to occur, the seal on the top reactor would be broken and hydrogen fluoride vapor would flow into the hopper causing severe corrosion problems and eventual equipment failure (21).

Hydrogen fluoride heating and condensing systems are affected by the same potential corrosion problems as those associated with the reactor system. An additional hazard is overheating and/or overpressure caused by a malfunction in the temperature control system.

3.3 REPACKAGING

Anhydrous hydrogen fluoride and hydrofluoric acid are repackaged for resale and further use. Aqueous hydrofluoric acid is typically repackaged into drums and carboys, while anhydrous hydrogen fluoride is commonly repackaged into cylinders. Hazards associated with this operation include overpressure, overfilling, mechanical damage, fire exposure, and chemical contamination.

A filling operation is usually carried out by transferring hydrogen fluoride from a bulk storage vessel using specially designed filling systems similar to those used for chlorine (22). Protective barriers are sometimes used to separate the transfer storage tank from the cylinder or drum being filled to prevent damage from shrapnel as a result of a possible rupture of the cylinder or drum (23).

Equipment used in repackaging operations should be constructed from materials compatible with hydrogen fluoride or hydrofluoric acid, depending on the operations. Relief systems are usually incorporated into the transfer system to prevent possible equipment ruptures. In addition, care usually is taken to prevent overfilling of drums and cylinders.

3.4 STORAGE AND TRANSFER

Anhydrous hydrogen fluoride is stored in pressure vessels because of its relatively low boiling point and high vapor pressure. Hydrogen fluoride is also stored in cylinders for small scale use and is shipped by tank car and tank truck. Figures 3-5 and Figure 3-6 show typical storage and transfer operations. These figures are only conceptual representations of storage and transfer operations. Actual transfer system will vary in the design and method of transfer. Moderate quantities of hydrogen fluoride may be stored as a pressurized and liquified gas. Larger quantities are usually stored at atmospheric pressure, as refrigerated liquids in single and double-walled horizontal cylindrical or spherical vessels. Vendors or process licensors should be consulted for detailed specifications on recommended storage facilities (8,24,25,26,27).

Transfer of the hydrofluoric acid to storage is accomplished using either pumps or compressed gas pressure. If compressed gas is used, it should first be dried to a moisture content equivalent to air at -22°F dew point to prevent corrosion of the storage and transfer vessels (8). For anhydrous hydrofluoric acid, nitrogen or hydrocarbon gas is usually used. If a hydrocarbon is used, air must be excluded to avoid a possible flammable mixture which would be a significant release hazard. If air is used, corrosion can occur as a result of oxygen dissolution in the acid, since hydrogen fluoride is commonly stored in carbon steel tanks.

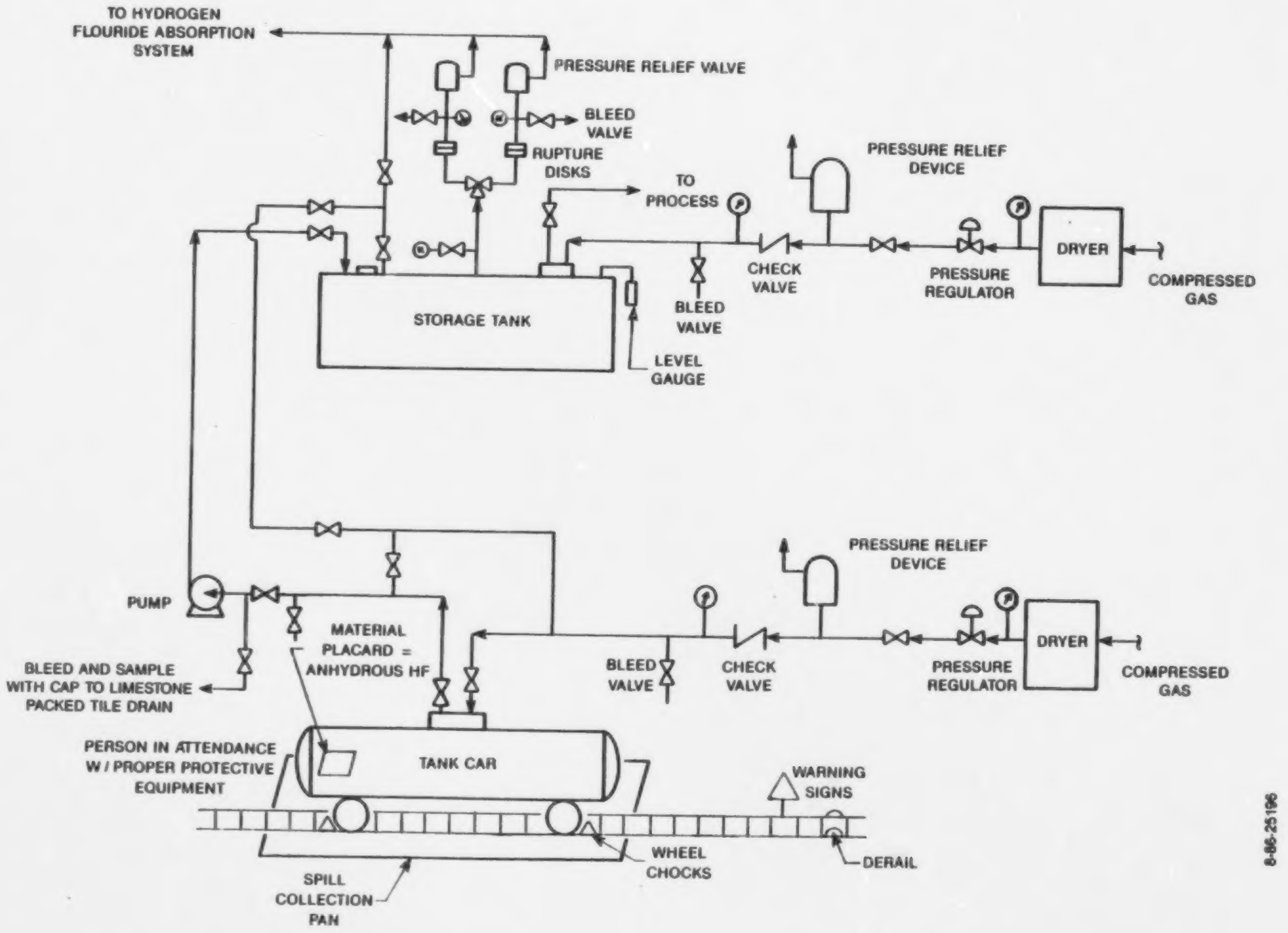
TO HYDROGEN FLOURIDE ABSORPTION SYSTEM
PRESSURE RELIEF VALVE
BLEED VALVE
RUPTURE DISKS
TO PROCESS
PRESSURE RELIEF DEVICE
CHECK VALVE
PRESSURE REGULATOR
DRYER
COMPRESSED GAS
BLEED VALVE
STORAGE TANK
LEVEL GAUGE
PRESSURE RELIEF DEVICE
PUMP
MATERIAL PLACARD = ANHYDROUS HF
BLEED AND SAMPLE WITH CAP TO LIMESTONE PACKED TILE DRAIN
BLEED VALVE
CHECK VALVE
PRESSURE REGULATOR
DRYER
COMPRESSED GAS
PERSON IN ATTENDANCE W / PROPER PROTECTIVE EQUIPMENT
TANK CAR
WARNING SIGNS
WHEEL CHOCKS
DERAIL
SPILL COLLECTION PAN
8-86-25196

Figure 3-5. Conceptual process diagram of hydrogen fluoride rail tank car unloading and tank storage facility.

Source: Reference 8

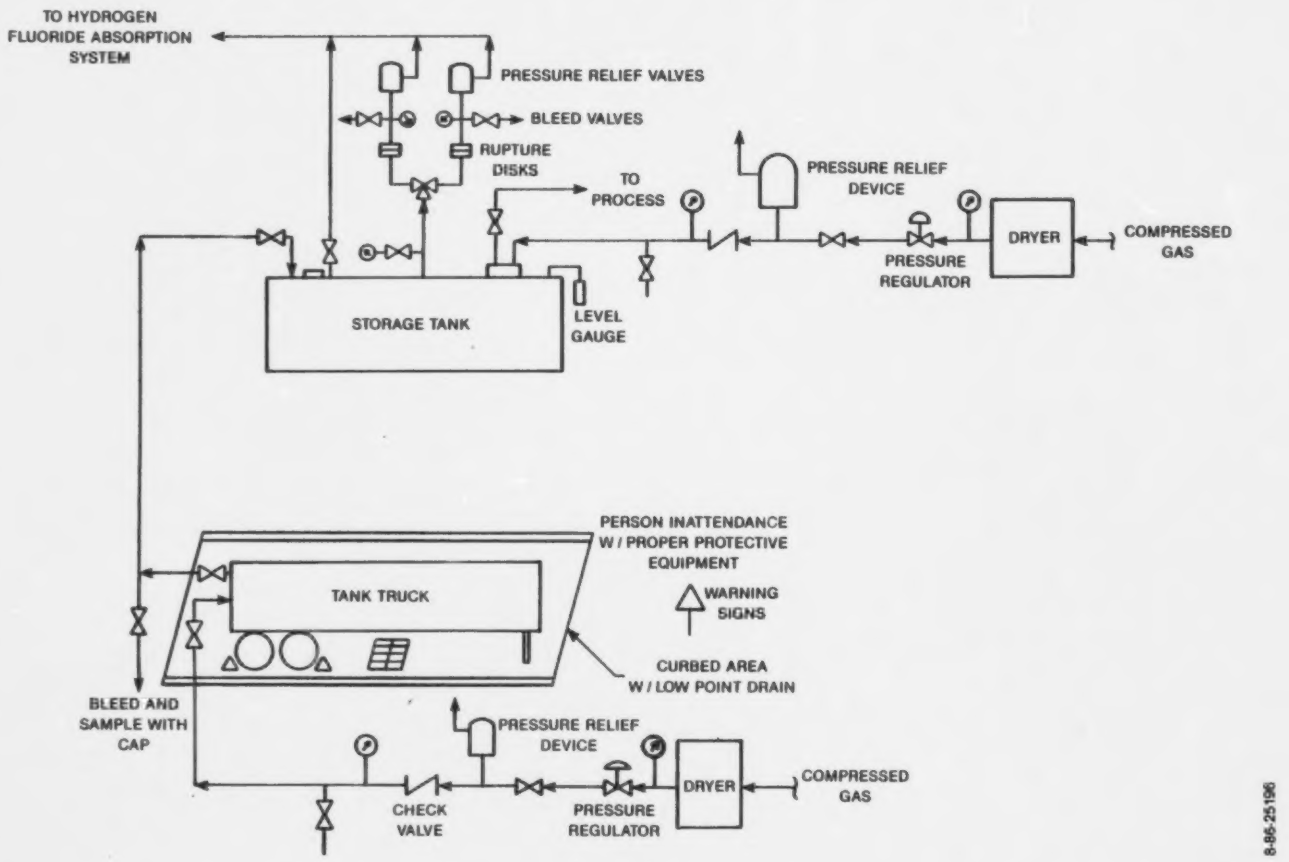
TO HYDROGEN FLUORIDE ABSORPTION SYSTEM
PRESSURE RELIEF VALVES
BLEED VALVES
RUPTURE DISKS
TO PROCESS
PRESSURE RELIEF DEVICE
DRYER
COMPRESSED GAS
PRESSURE REGULATOR
STORAGE TANK
LEVEL GAUGE
PERSON INATTENDANCE W / PROPER PROTECTIVE EQUIPMENT
WARNING SIGNS
TANK TRUCK
CURBED AREA W / LOW POINT DRAIN
BLEED AND SAMPLE WITH CAP
PRESSURE RELIEF DEVICE
DRYER
COMPRESSED GAS
CHECK VALVE
PRESSURE REGULATOR
8-86-25196

Figure 3-6. Conceptual process diagram of hydrogen fluoride tank truck unloading and tank storage facility.

Source: Reference 8

For safety reasons, pump transfer is commonly preferred over compressed gas transfer. The pumps most commonly used are centrifugal, rotary, or positive displacement, depending on the specific situation. Sealless pumps may be required for some applications. In addition, self-priming pumps are commonly used since they avoid the hazards that can be associated with priming the pump.

SECTION 4
PROCESS HAZARDS

Both anhydrous hydrogen fluoride and hydrofluoric acid can be used safely in appropriate processing and storage equipment. However, when exposed to the atmosphere, hydrogen fluoride vaporizes readily and, because of its strong affinity for water, combines with moisture in the air to form hydrofluoric acid. This acid can be detected in air by its white fumes, pungent odor and irritant property.

Hydrogen fluoride releases can originate from many sources including leaks or ruptures in vessels, piping, valves, instrumentation connections, and process machinery such as pumps and compressors.

Potential hydrogen fluoride releases may be liquid or vapor. Liquid spills can occur when anhydrous fluoride is released at or below its boiling point of 67°F or when a sudden release of hydrogen fluoride above this temperature results in vapor flashing, which cools the remainder of the chemical to 67°F. Direct releases of vapor or gas also can occur. Liquid spills of hydrofluoric acid can release some hydrogen fluoride as well. However, the vapor pressure resulting from the concentrated acid is considerably less than the vapor pressure of pure hydrogen fluoride. Nonetheless, the threat from the acid should not be overly discounted, especially if spills occur on hot surfaces where evaporation rates are high.

4.1 POTENTIAL CAUSES OF RELEASES

Failures leading to accidental releases may be broadly classified as due to process, equipment, or operational causes. This classification is for convenience only. Causes discussed below are intended to be illustrative, not exhaustive. A more detailed discussion of possible causes of accidental releases is planned in other portions of the prevention reference manual series of which this present manual is a part.

4.1.1 Process Causes

Process causes are related to the fundamentals of process chemistry, control, and general operation. Possible process causes of a hydrogen fluoride release include:

- Excess olefin feed to an alkylation reactor leading to excessive exothermic reaction, combined with failure of the cooling system;
- Backflow of process reactants to a hydrogen fluoride feed tank;
- Inadequate water and sulfur removal from hydrocarbon feeds to the alkylation process over a long period of time leading to progressive corrosion;
- Excess feeds in any part of the system leading to overfilling or overpressuring equipment;
- Loss of condenser cooling in distillation units;
- Loss of temperature control in cooling and heating units; and
- Overpressure in hydrogen fluoride storage vessels due to overheating or overfilling. These situations may be caused by exothermic reactions from contamination, fire exposure, or unrelieved overfilling.

4.1.2 Equipment Causes

Equipment causes of accidental releases result from hardware failures. Some possible causes include:

- Excessive stress due to improper fabrication, construction, or installation;

- Failure of vessels at normal operating conditions due to weakening of equipment from excessive stress, external loadings, or corrosion. Overheating is also a possibility, especially for alkylation reactors and distillation columns;

- Mechanical fatigue and shock in any equipment. Mechanical fatigue could result from age, vibration, or stress cycling, caused by pressure cycling, for example. Shock could occur from collisions with moving equipment such as cranes, or other equipment in process or storage areas;

- Thermal fatigue and shock in alkylation reactors, heat exchangers, and distillation columns;

- Brittle fracture in any equipment, but especially in carbon steel equipment subjected to extensive corrosion where hydrogen embrittlement from hydrogen release by hydrogen fluoride attack may have occurred. Equipment constructed of high alloys, especially high strength alloys selected to reduce the weight of major process equipment, might be especially sensitive where some corrosion has occurred, or severe operating conditions are encountered;

- Creep failure in equipment subjected to extreme operational upsets, especially excess temperatures. This can occur in equipment subjected to a fire that may have caused damage before being brought under control; and

- All forms of corrosion. External corrosion from fugitive emissions of hydrogen fluoride could lead to equipment weakening. Stress corrosion cracking is also a possibility since this is characteristic of certain metals exposed to halogens.

4.1.3 Operational Causes

Operational causes of accidental releases are a result of incorrect operating and maintenance procedures or human errors (i.e., not following correct procedures). These causes include:

- Overfilled storage vessels;

- Improper process system operation;

- Errors in loading and unloading procedures;

- Inadequate maintenance in general, but especially on water removal unit operations, and pressure relief systems and other preventive and protective systems;

- Lack of inspection and non-destructive testing of vessels and piping to detect corrosion weakening;

- Incomplete knowledge of the properties of a specific chemical; and

- Incomplete knowledge of the process or chemical system.

SECTION 5
HAZARD PREVENTION AND CONTROL

5.1 GENERAL CONSIDERATIONS

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices. These practices apply to the design, construction, and operation of facilities where hydrogen fluoride is stored and used. Considerations in these areas can be grouped as follows:

- Process design considerations,
- Physical plant design considerations,
- Operating and maintenance practices, and
- Protective systems.

In each of these areas, consideration must be given to specific factors that could lead to a process upset or failure which could directly cause a release of hydrogen fluoride to the environment, or result in an equipment failure which would then cause the release. At a minimum, equipment and procedures should be examined to ensure that they are in accordance with applicable codes, standards, and regulations. In addition, stricter equipment and procedural specifications should be in place if extra protection against a release is considered appropriate.

The following subsections discuss specific considerations regarding release prevention; more detailed discussions will be found in a manual on control technologies, part of this manual series.

5.2 PROCESS DESIGN

Process design considerations involve the fundamental characteristics of the processes which use hydrogen fluoride. These considerations include an evaluation of how deviations from expected process design conditions might initiate a series of events that could result in an accidental release. The primary focus is on how the process is controlled in terms of the basic process chemistry, and the variables of flow, pressure, temperature, composition, and quantity. Additional considerations may include mixing systems, fire protection, and process control instrumentation. Modifications to enhance process integrity may result from review of these factors and would involve changes in quantities of materials, process pressure and temperature conditions, the unit operations, sequence of operations, the process control strategies, and instrumentation used.

Table 5-1 shows the relationship between some specific process design considerations and individual processes described in Section 3 of this manual. This does not mean that other factors should be ignored, nor does it mean that proper attention to just the considerations in the table ensures a safe system. The considerations listed, and perhaps others, must be properly addressed if a system is to be safe, however.

The most significant considerations are aimed at preventing overheating and overpressuring systems containing hydrogen fluoride. If hydrogen fluoride is fed from a storage vessel under its own vapor pressure, the primary means of overpressure would be from overheating. Where hydrogen fluoride might be fed by nitrogen padding of a storage vessel, or through pumps or compressors, overpressuring could occur without overheating. Equipment failure without overpressure is possible if corrosion has weakened process equipment. Temperature monitoring is important, not only because of a potential overpressure or equipment weakening due to overheating, but also because hydrogen fluoride's corrosiveness increases with temperature.

TABLE 5-1. SOME PROCESS DESIGN CONSIDERATIONS FOR PROCESSES INVOLVING HYDROGEN FLUORIDE

Process Design Consideration	Process or Unit Operation
Contamination (with water and sulfur especially)	All
Flow control of hydrogen fluoride feed	All
Temperature sensing and heating media flow control	Hydrogen fluoride reactor, uranium tetrafluoride reactor, chlorofluorocarbon reactors, distillation and stripping column reboilers
Temperature sensing and cooling medium flow control	Alkylation reactors, aluminum fluoride reactors, distillation and stripping column condensors
Adequate pressure relief	Storage tanks, reactors, distillation and stripping columns, heat exchangers
Mixing	Alkylation reactors
Corrosion monitoring	All, but especially recycle circuits
Temperature monitoring	All reactors, alkylation, stripping column, and distillation column reboilers
Level sensing and control	Storage tanks, settlers in alkylation and chlorofluorocarbon processes

5.3 PHYSICAL PLANT DESIGN

Physical plant design considerations include equipment, siting and layout, and transfer/transport facilities. Vessels, piping and valves, process machinery, instrumentation, and factors such as location of systems and equipment must all be considered. The following subsections cover various aspects of physical plant design beginning with a discussion of materials of construction.

5.3.1 Equipment

Materials of Construction--

The proper selection of materials of construction for hydrogen fluoride service is dictated by conditions which directly and indirectly affect corrosion. Temperature, pressure, moisture content, flow velocity, aeration, and impurities such as sulfur compounds are important considerations in determining the appropriate materials. Table 5-2 presents a list of possible materials of construction for hydrogen fluoride service (24). The National Association of Corrosion Engineers (NACE) also provides detailed information concerning the materials of construction for hydrogen fluoride service (28).

For anhydrous hydrogen fluoride at temperatures up to 150°F, fully killed mild steel, steel deoxidized using silicon and/or aluminum, is generally used (e.g., ASTM A516, Grade 60 or 70). However, hydrogen blistering can occur if plates contain lamination defects. Reducing the sulfur content to a maximum level of 0.010% or using inclusion shaped controlled steels helps to eliminate blistering. Another possible problem is hydrogen cracking of hardened steels. Base metals, welds, and heat affected zones should be limited to hardness less than HRC 22 to avoid the problem (28). This includes the use of low hardness bolts such as ASTM A193 Grade B7M instead of B7 (28). For temperature greater than 150°F, nickel-copper Alloy 400 and nickel-chromium-molybdenum alloys are often used. However, nickel-copper alloys may stress corrosion crack if humid

TABLE 5-2. CHARACTERISTICS OF MATERIALS OF CONSTRUCTION IN HYDROGEN FLUORIDE AND HYDROFLUORIC ACID SERVICE

HYDROGEN FLUORIDE OR STRONG ACID (70% OR OVER)

Satisfactory

Copper*
Monels**
Inconel
Low Carbon Steel (to 150°F) Hastelloy Alloys B, C D Nickel Ni-resist Carpenter 20 Durimet 20 Magnesium Chlorimet 2 & 3 Karbate (70%) Polyethylene Unplasticized Polyvinyl Chloride Saran-Lined Steel Pipe (for 70% <120°F) Fluorocarbons (TFE, CFE & FEP) Platinum Molybdenum**

Unsatisfactory

- Yellow Brass
- Lead
- High Silicon Iron Alloys
- Cast iron
- Aluminum
- Stainless Steels
- Tantalum
- Titanium
- Zirconium
- Low Silver Brazing Alloys
- Rubber, Natural & Synthetic
- Glass & Ceramics
- Epoxies
- Asbestos

DILUTE ACIDS (UNDER 70% HF)

Satisfactory

- Monels**
- Copper*
- Yellow Brass*
- Nickel (over 10%, <212°F)
- Lead (Chemical Grade <60%, to b.p.)
- Silver
- Carpenter 20
- 70-30 Copper Nickel Alloy
- Magnesium (<185°F)
- Hastelloy Alloys B,C&D
- Karbate
- Neoprene (<50%, <140°F)
- Unplasticized Polyvinyl Chloride
- Rubber-Lined Steel (<60%, <180°F)
- Butyl-Rubber-Lined Steel (<60%, <180°F)
- GR-S (<60%, <180°F)
- Carbon-Filled Sulfur Cement
- Saran-Lined Pipe
- Polypropylene Vinylidene Fluorides
- Fluorocarbons (TFE, CFE & FEP) Platinum

Unsatisfactory

- Steel
- Stainless Steels
- Ni-resist
- Cast iron
- High Silicon Iron Alloys
- Glass & Ceramics
- Aluminum
- Inconel (<10%, <170°F)
- Wood
- Tantalum
- Titanium
- Zirconium
- Asbestos

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*SO_2 and air free.

**May be unsuitable under aerating conditions.

Note: This table does not include exceptions to satisfactory service due to temperature, concentration, velocity, etc. It is given here to provide a starting point for selecting materials, but a given materials acceptability for a certain application should be confirmed by other references before it is used.

air is in contact with the acid or if substantial aeration in the process stream occurs.

Hydrofluoric acid solutions of concentrations greater than 70% can also be handled in fully-killed mild steel up to 100°F provided that the steel has a passivation film on the surface and velocity through the equipment is less than 1.0 foot per second (8). The passivation iron fluoride film results from a reaction between the steel and the acid and provides a protection from further corrosion. When velocities are in excess of 1.0 foot per second, the passivation film is eroded (8). In addition, copper and its alloys are not suitable where anhydrous hydrogen fluoride flows at high velocity. Materials of greater acid resistance must be used in such service.

For anhydrous hydrogen fluoride or concentrated hydrofluoric acid solutions (greater than 70%) systems, carbon steel pipe is commonly used. ASTM A53 seamless or A106, Grade A or B steel piping is often selected (3). For piping up to one inch, the pipe should be welded steel, and for sizes of greater diameter, the pipe should be seamless steel (24). The flanges commonly used are of ANSI Class[a] forged steel, raised face, welding neck, and ASTM A-105 or A-181, (24). For concentrations less than 70% hydrogen fluoride, piping is commonly lined with polypropylene, unplasticized polyvinylchloride, polyvinylidenechloride, polyvinylidinefluoride, or tetrafluoropolyethylene (TFE) to prevent corrosion (2). Materials which are not recommended include aluminum, titanium, tin, ordinary grey iron, malleable iron fittings, general purpose valves, and porcelain valves.

Gaskets constructed of nickel-copper Alloy 400 and TFE are commonly used for hydrogen fluoride service. These materials provide a needed resistance to corrosion at all hydrogen fluoride concentration levels.

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[a] ANSI Class refers to pressure ratings at specified temperatures as set by the American National Standards Institute (ANSI). For a carbon steel flange, Class 150 means a 150 psig pressure rating at 500°F, and Class 300 means a 300 psig pressure rating at 850°F.

Bolts with adequate resistance to hydrogen stress corrosion cracking must be used in holding the flanges together. Alloy steel studs with heavy hex nuts are commonly used. Several types of bolts are often used in hydrogen fluoride service including: ASTM A-307, Grade B, mild steel; ASTM A-193, Grade B-7-M, alloy steel with maximum Rockwell C hardness of 22; ASTM A-193, Grade B-8, Class 2, 304 stainless steel with a maximum Rockwell C hardness of 34 (24). If a flange begins to leak, bolts are usually replaced immediately.

Hydrofluoric acid in concentrations less than 70% must be handled and stored in nonferrous materials. Since nickel-copper Alloy 400 is resistant to hydrofluoric acid in almost the entire concentration range, it is commonly used for storage of hydrogen fluoride. In addition, nickel-chromium-iron alloys and nickel-chromium-molybdenum alloys do not show corrosion in 40-60% hydrofluoric acid up to 206.6°F (8).

Glass and silicate ceramics should never be used with hydrogen fluoride or hydrofluoric acid at any concentration.

Vessels--

A variety of storage and process vessels are used in hydrogen fluoride service. Examples include small storage cylinders, chemical reactors, separation columns, heat exchangers, and large storage tanks. Each type of vessel has certain specifications under various codes and standards which are supposed to be adhered to in design and fabrication.

Hydrogen fluoride storage vessels range in size from 150 lb pressure cylinders for small scale use up to several thousand metric ton pressurized spherical storage tanks used by producers. Pressurized storage tanks varying from 100-200 tons are typically used to store hydrogen fluoride for use in chemical processes. In addition, refrigerated tanks varying in size from 100-250 tons are also used for hydrogen fluoride storage. The shell of a refrigerated storage tank is covered by refrigeration coils and insulation. These coverings must be removed before the tank can be inspected for signs of external corrosion or wear. The shell of a pressurized tank does not need to be covered, and thus the exterior surface can be easily inspected. For this reason, most producers of hydrogen fluoride prefer to use pressurized storage in place of refrigerated storage. The hazard associated with pressurized hydrogen fluoride is felt to be more than offset by the ability to regularly inspect the tank. As a result of the relatively large inventories contained in hydrogen fluoride storage vessels, they represent one of the most hazardous parts of a hydrogen fluoride process facility.

In general, anhydrous hydrogen fluoride and hydrofluoric acid storage tanks should be designed and built in accordance with the ASME Code for Unfired Pressure Vessels. Special considerations may be as discussed in the code for lethal materials, or even stricter standards may be appropriate.

As stated earlier, the usual material for hydrogen fluoride storage vessels is mild steel. Because of the potential release of hydrogen during corrosive attack by moist hydrogen fluoride, welding processes are usually carefully controlled to avoid heat-affected zone hardness which can lead to hydrogen stress cracking. Shielded arc welding with double butt-welded longitudinal seams and single butt-welded girth seams with seal welds on the inside is commonly used for vessels, including those in hydrogen fluoride service.

A minimum design pressure for these storage tanks is at least 50 psig working pressure, with a requirement that the tanks be tested at 1.5 times the working pressure prior to use. A minimum corrosion allowance of at least a 1/8 inch on both the shell and heads is typically added to the thickness specified by the ASME code for the specified design pressure.

Vessel nozzles are constructed of mild steel with ANSI Class 300 or greater forged steel weld neck flanges. Except for single, flanged, bottom clean-out drains, bottom outlet nozzles are not often used since there is a greater risk of losing the entire tank contents as the result of valve or line failure. Where they are used, nozzles are usually double valved as a precautionary measure. The following nozzles are usually specified for mounting on top of the tank (24):

- One 3- or 4-inch nozzle for insertion of a dip pipe for removal of hydrogen fluoride from the tank;
- Two 2-inch nozzles: one for filling the tank and the other for a pressure relief device; and
- Three 1-inch nozzles: one for a dry air supply to pad the hydrogen fluoride out, one for a vent to a caustic scrubber, and the last for a pressure gauge.

Specific release prevention considerations for vessels include: overpressure protection, temperature control, and corrosion prevention. Relief devices are not usually provided for 150-pound cylinders. These cylinders are built to withstand very high pressures and must be kept from fire exposure, contamination, and mechanical damage. Larger vessels are usually equipped with pressure relief valves as are tank trucks and rail cars. Process vessels are usually protected by pressure relief valves and/or rupture discs. Since hydrogen fluoride tends to corrode pressure relief valves, they are frequently separated from the hydrogen fluoride by a rupture disc. The pressure relief valve is set to relieve slightly above the design working pressure of the vessel, but well below the maximum allowable working pressure.

Pressure relief valves and rupture discs are designed to prevent explosion by allowing a controlled release of overpressurized contents. These relief systems are usually sized for flashing liquid caused by:

- Fire exposure (NFPA 30),
- Thermal expansion,

- Internal reaction/decomposition, and
- Excess supply rates.

Relief piping must be sized for adequate flow. To avoid direct discharge to the atmosphere, an overflow tank might be provided for overpressured liquid. If there is a possibility that overpressuring may occur due to causes other than liquid thermal expansion, or where there is no overflow receiver, the vessels should be relieved to either a point in the process which can handle the discharge flow, or to a gas absorption system.

The foundations and supports for vessels are important design considerations, especially for large storage vessels and tall equipment such as distillation columns. Supports for storage tanks containing hydrogen fluoride are usually concrete saddles. Tubular support legs are usually avoided. The supports must be protected from possible hydrofluoric acid contact since rapid corrosion can result from dilution of the acid with moisture in the air. Fugitive emissions of hydrogen fluoride can lead to significant external corrosion of supports and bolting. These supports should be protected by fugitive emissions control and regular maintenance of structural members. Surface coatings of mastics or polymers may also help retard external corrosion.

Cylinder storage of hydrogen fluoride is common where small to moderate quantities are required. A hood with forced ventilation is commonly used with hydrogen fluoride cylinders. Cylinder storage temperatures should not exceed 130°F and cylinders should be located away from sources of heat (25). Trap or check-valves are commonly inserted in transfer lines to prevent hazardous backflow into the cylinder. In addition, pressure-reducing regulators are used when connecting cylinders to lower pressure piping systems to prevent overpressure with leaks or rupture of downstream line (25). Air pressure is usually not used to transfer hydrogen fluoride from cylinders since corrosion resulting in the generation of hydrogen gas can occur. When pressure transfer (above the vapor pressure of hydrogen fluoride) is needed, nitrogen or other inert gases are usually used. Cylinders also may be slightly heated using hot water. However, care must be taken to guard against overpressure. Cylinders are usually examined periodically for signs of valve or other leakage and external deterioration. Cylinders which have been stored for long periods of time are usually safely vented prior to use, since they may contain hydrogen gas. Complete details on cylinder storage are provided in hydrogen fluoride manufacturer's literature (25,26).

The reactors used in hydrogen fluoride related processes represent possible sources of major releases since they contain a large portion of the anhydrous hydrofluoric acid used in their respective processes. These reactors must, therefore, be properly constructed of appropriate materials of construction.

The feed to the reactors must be dry since moisture accelerates the corrosion rate of materials used in construction (e.g., carbon steel). Provisions should be made for exclusion of moisture during any process shutdowns, or purging of the reactors at shutdown and before startups.

Since the alkylation reaction is exothermic, a heat-exchange-tube bundle is commonly used to cool the alkylation reactor contents. Water is the cooling medium. This equipment must be designed to prevent water leakage into the acid section of the reactor. Provisions must be made for corrective action to be taken if such leakage should occur. Common precautions include ensuring that the water pressure is lower than the process fluid pressure, and monitoring the cooling water for pH. If leakage should then occur, the acid would enter the water system and be detected by the pH monitoring.

A pressure relief system along with a means of gas purging is also sometimes incorporated into the reactor designs since hydrogen gas may build up as a result of corrosion. All vents should be routed to a caustic scrubber.

Distillation and stripping columns present significant release hazards because they contain large amounts of hydrogen fluoride in pure form and have a heat input. The conditions under which this equipment operates (especially the column reboilers and bottoms pumps) are severe and as a result these areas are potential sites for a release.

If cooling in a condenser is lost, overpressure may occur. Thus, it is necessary to use pressure relief valves to protect against leaks and ruptures which can result from overpressure. Relief protection is also necessary in the event of a fire to protect from overpressure. Likewise, loss of steam to the reboilers can result in underpressure in the column.

Columns used in hydrogen fluoride service must be constructed from the suitable materials mentioned in Section 5.3.1. The columns should be properly supported, taking into consideration expansion and contraction as a result of temperature changes, corrosion, and possible wind loadings.

Piping--

As with hydrogen fluoride vessels, hydrogen fluoride pipework design must reflect the pressure, temperature, and corrosion concerns associated with use of the chemical. Careful attention must be paid to pipework and associated fittings since failures of this type of equipment are major contributors to accidental releases of chemicals. Regardless of the physical state of the hydrogen fluoride, there are some general guidelines for hydrogen fluoride piping systems. The first is simplicity of design; the number of joints and connections should be minimized. In addition to being securely supported, pipes should be sloped, with drainage at the low points. Piping should be constructed so as to allow room for thermal expansion of the pipe and should be protected from exposure to fire and high temperatures. Placement of valves should ensure isolation of leaking pipes and equipment.

A chief concern in liquid hydrogen fluoride lines is overpressure due to thermal expansion of the chemical or pressure pulses caused by rapid valve closure. These pressures can be sufficient to rupture the pipe. Where applicable, an expansion chamber, such as the one shown in Figure 5-1, may be installed to prevent such a rupture. An expansion chamber device typically consists of a rupture disc and a receiver chamber which can hold about 20-30% of the protected line's capacity. The chamber is equipped with a pressure indicator or alarm switch set to function upon disk rupture. The chamber should be constructed in accordance with Section VIII of the ASME Code for Unfired Pressure Vessels (29).

Another concern in liquid hydrogen fluoride systems is low temperature toughness. Material selection must take this into account and should be resistant to brittle fracture over the entire range of process conditions.

The correct design and use of pipe supports is essential to reduce overstress and vibration which could lead to piping failure. The supports should be designed to handle the load associated with the pipe, operating and testing medium, insulation, and other equipment. Factors which must be considered include thermal expansion and contraction, vibrations caused by pumping and fluid flow, bending moments as a result of overpressure in the pipe, and external loads such as winds or ice accumulation.

Piping networks are usually pressure tested at a minimum, to meet the requirements specified by ANSI code B31.3 (32). If a gas is used, it must be dry to prevent corrosion and resulting hydrogen gas formation. If water is used, the piping must be drained and blown dry before use.

As a result of the possible buildup of hydrogen gas from corrosive effects and the relatively low boiling point of hydrogen fluoride, rupture due to hydrostatic pressure is possible. Protection against this is commonly provided by installing a pressure relief valve, rupture disk, or a suitably designed, operated, and maintained expansion chamber (23).

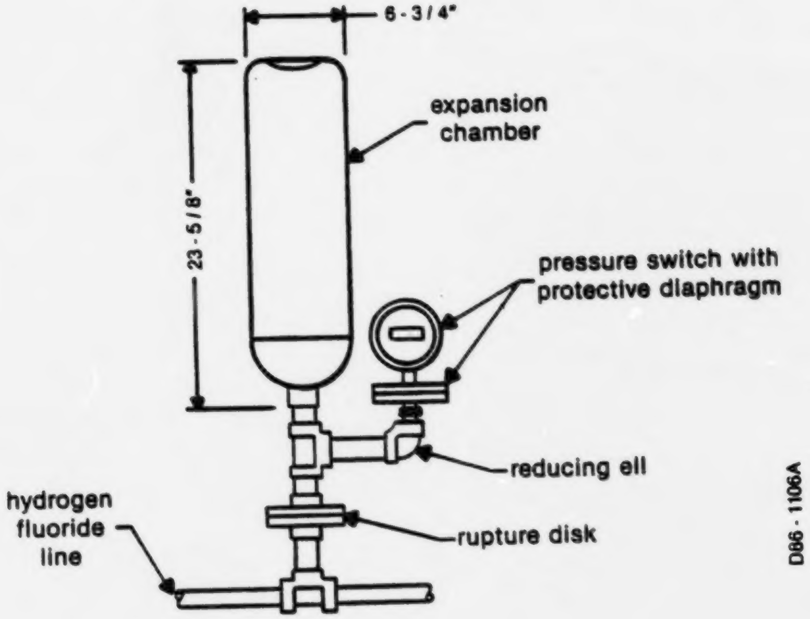

6-3/4"
23-5/8"
expansion chamber
pressure switch with protective diaphragm
reducing ell
hydrogen fluoride line
rupture disk
D86-1106A

Figure 5-1. Concept of a liquid hydrogen fluoride expansion chamber.

Source: Reference 29

All piping should be situated away from fire and fire hazards since the presence of hydrogen gas could trigger an explosion. If possible, piping carrying hydrogen fluoride should not be routed near other processes or piping networks which might present an external threat (e.g., piping carrying highly corrosive materials, high pressure processes). Pipe flanges should be situated so as to minimize potential hazards from drips and small leaks since these could cause rapid external corrosion. In addition, the piping network should be protected from possible impact and other structural damage.

Valves in hydrogen fluoride service are discussed in a number of references (8,23,24,30). Several types of valves including gate, globe, ball, relief, excess flow, and check configurations are used in hydrogen fluoride-containing systems. Valves of all sizes and for all pressure ranges used in hydrogen fluoride alkylation processes must be approved by one of the major hydrofluoric acid alkylation process licensers (i.e., U.O.P., Phillips Petroleum and Chevron) before being used (30).

Nickel-copper Alloy 400 is commonly used for all valve trim parts (i.e., seats, disks and stems) because of its resistance to the corrosive properties of hydrofluoric acid. A problem with valve trim materials is that they have thermal expansion coefficients which exceed those of cast or forged carbon steel and as a result often become distorted, causing leaks. Often this is solved by either closing the valve more tightly or inserting an acid compatible ring either in or alongside the trim material in the seat or disk. For anhydrous hydrogen fluoride, the valve bodies can be cast steel. For hydrofluoric acid (<70% concentration) nickel-copper Alloy 400 valve bodies are often used.

Hydrofluoric acid will react with carbon steel and to a lesser extent with copper-nickel alloys that contain small amounts of iron to form ferric fluoride. Thus, hydrogen fluoride valves must have appropriate clearances at critical interfaces such as wedge/body guides and stem back-seat bushings to prevent the valves from becoming inoperable from ferric fluoride deposits.

Check valves are a primary means of preventing undesired back or reverse flows. They are typically mounted vertically on hydrogen fluoride storage tanks so that forward flow is required to lift and open them. Such valves can prevent undesired materials from entering hydrogen fluoride-containing equipment and also prevent possible explosions as a result of backups into tanks. Check valves are also used widely on the pump discharges to prevent undesired backflow which could render a pump inoperable and eventually result in a hazardous release. Nickel-copper alloy ball check valves are commonly used in hydrogen fluoride service. Dual check valves in series are commonly used in sensitive/severe service areas. A power operated control valve with suitable instrumentation may be used as a substitute for a check valve.

Pressure relief devices should be installed on all hydrogen fluoride-containing vessels where the chemical can be blocked in. Such devices are set to relieve at a pressure approximately equal to the design pressure (which is greater than the normal operating pressure) for each specific piece of equipment. Where fires are likely, in alkylation units for example, the relief system should also be designed for fire relief, which tends to require a larger pressure relief capacity.

Process Machinery--

Process machinery refers to rotating or reciprocating equipment that may be used in the transfer or processing of hydrogen fluoride or hydrofluoric acid. This includes pumps and compressors which may be used to move liquid or gaseous hydrogen fluoride where gas pressure padding is insufficient or inappropriate.

Pumps--Many of the concerns and considerations for hydrogen fluoride piping and valves also apply to pumps. To assure that a given pump is suitable for a hydrogen fluoride service application, the system designer should obtain information from the pump manufacturer certifying that the pump will perform properly in this application.

Pumps should be constructed with materials which are resistant to hydrogen fluoride at operating temperatures and pressures. They should be installed dry and oil-free. It is especially important that their design not allow hydrogen fluoride or lubricating oil to enter seal chambers where they may contact one other. Net positive suction head (NPSH) considerations are especially important for hydrogen fluoride since pumping the liquid near its boiling point may be common (hydrogen fluoride boils at near ambient conditions). The pump's supply tank should have high and low level alarms; the pump should be interlocked to shut off at low supply level or low discharge pressure. External pumps should be situated inside a diked area, and should be accessible in the event of a tank leak.

The type of pump selected depends on pumping requirements and operating conditions. Centrifugal, rotary, and positive displacement are used to pump hydrogen fluoride. Sealless pumps are used for some applications. The pumps used should be constructed of suitable materials such as carbon steel, nickel-chromium-molybdenum and nickel-copper alloys which are resistant to hydrogen fluoride corrosion. These pumps are subject to shaft seal leakage, so real rings made of polyvinylidenefluoride, nickel-chromium-molybdenum alloy and nickel-copper Alloy 400 are often used to eliminate this problem. Close-fitting moving parts should not be constructed of steel since the ferric fluoride film produced by the corrosion of steel can cause the parts to freeze up. In addition, Type 400 stainless steels, cast iron, and hardened steels should never be used.

In some situations, the potential for seal leakage rules out the use of standard rotating shaft seals. One solution is to use pump types which isolate the seals from the process stream. The seals are typically cartridge canister double type (31). The buffer fluid between the mechanical seals is commonly light oil. Another solution is to use pump types which eliminate shaft seals altogether such as canned-motor pumps, vertical submersible pumps, magnetically coupled pumps and diaphragm pumps (4,23).

Canned motor pumps are centrifugal units in which the motor housing is interconnected with the pump casing. Here, the process liquid actually serves as the bearing lubricant. An alternative concept is the vertical pump often used on storage tanks. These pumps consist of a submerged impeller housing connected by an extended drive shaft to the motor. The advantages of this arrangement are that the shaft seal is above the maximum liquid level (and is therefore not wetted by the pumped liquid) and the pump is self priming because the liquid level is above the impeller.

Pumps using stuffing boxes and packing should be provided with double-packed seal chambers designed to prevent hydrogen fluoride from contacting any reactive material. These chambers can be purged with an appropriate inert fluid such as dry and oil-free nitrogen, or a suitable seal liquid. The seal gas pressure should exceed the tank pressure by an appropriate margin. A seal fluid back-up system should be considered (31).

Magnetically-coupled pumps replace the drive shaft with a rotating magnetic field as the pump-motor coupling device. Diaphragm pumps are positive displacement units in which a reciprocating flexible diaphragm drives the fluid. This arrangement eliminates exposure of packing and seals to the pumped liquid.

For metering service, diaphragm pumps are commonly used. The main advantage of this type of pump is none of the packing and seals are exposed to the pumped liquid. However, a major consideration in the application of such pumps is that at some point, diaphragm failure will probably occur. Such a failure could lead to a release. These pumps may have a pressure relief valve on the outlet, bypassing to the suction.

Improper operation of pumps as a result of cavitation, running dry, and deadheading can cause damage and failure of pumps. Cavitation can be a problem in pumping because of low boiling point of hydrogen fluoride and tendency to vaporize easily. If cavitation is allowed to occur, pitting and eventual serious damage to the impeller can result. Running a pump dry as a result of loss of head in a feed tank, for example, can seriously damage a pump. Finally, pumping against a closed valve can have serious ramifications. A pump bypass or kick-back are useful in avoiding such an occurrence. Failure of a pump, for whatever reason, can eventually lead to a hazardous release.

Centrifugal pumps often have a recycle loop back to the feed container which prevents overheating if the pump is deadheaded. This is an important consideration in hydrogen fluoride systems since hydrogen fluoride corrosiveness increases rapidly with increasing temperature. Deadheading is also a concern with positive displacement pumps. To prevent rupture, positive displacement pumps commonly have a pressure relief valve which bypasses to the pump suction. Because of the probability of eventual diaphragm failure, the use of diaphragm pumps should be carefully considered in view of this hazard potential.

Pumps are not always necessary; in many circumstances, liquid hydrogen fluoride is moved by pressure padding. With hydrogen fluoride cylinders and ton-containers, the liquid may be displaced from the vessel by the force of hydrogen fluoride vapor pressure. As discussed earlier, this process is temperature dependent. With other types of vessels, an inert gas such as dry nitrogen may be used to force liquid from the tank. Padding system designs must reflect the operating conditions and limitations (e.g., required flow rate) and therefore must be custom designed for a process.

Compressors--Reciprocating, centrifugal, liquid-ring rotary, and non-lubricated screw compressors are used with hydrogen fluoride. Details of such compressors used with hydrogen fluoride are discussed in the technical literature (4,31).

Like pumps, compressors have the potential for heat buildup and shaft seal leakage. Heat sources in a compressor include the heat of compression as well as the heat generated through mechanical friction. Heat buildup in hydrogen fluoride compressors is a particular concern because hydrogen fluoride's corrosion increases with increasing temperature. Most multistaged compressors can be equipped with intercoolers which limit heat buildup and increase compressor efficiency by reducing the volume of gas going to the next compression stage. Both air and water cooling are used, but water systems must be designed to prevent leakage and contact of water with hydrogen fluoride.

While it is often possible to avoid using rotary shaft seals with hydrogen fluoride pumps, compressors in hydrogen fluoride service usually require special seals such as double labyrinth seals. These seals have a series of interlocking touch points which, by creating many incremental pressure drops, reduce total leakage. Also, to further reduce leakage, dry air is injected into the seal. In the event of deadheading, a compressor discharge can have a pressure relief mechanism which vents to the compressor inlet or to a scrubber system. The former appears to be satisfactory for a short term downstream flow interruption. Where a sustained interruption might occur, relief to a scrubber system would be safer. Positive displacement compressors and pumps must always be equipped with overpressure relief as close to the discharge as possible (non-isolatable).

Miscellaneous Equipment--

Pressure Relief Devices--Information on specific relief valve types for hydrogen fluoride service is not readily available. Some characteristics for chlorine service seem to apply for hydrogen fluoride, however. For vessels, an acceptable relief valve is of angle body construction with a closed bonnet and a screwed cap over the adjusting screw. These valves are normally used in combination with a rupture disc or a breaking pin assembly. Typical valve construction materials include a cast carbon steel body; a nickel plated steel spring; and nickel-copper or nickel-chromium-molybdenum alloy nozzle, disc adjusting ring, nozzle ring, and spindle guide. The inlet flange should be ANSI Class 300 or greater and the outlet flange should be ANSI Class 150 or greater. Valves of this construction which also have Viton® "O" ring seat seals need not have a rupture disc or breaking pin. Other types of pressure relief devices are acceptable as long as they are constructed of materials suitable for hydrogen fluoride service and meet the general requirements of the ASME boiler and Pressure Vessel Code, Section VIII, Division 1 (26).

Rupture discs are constructed of appropriate hydrogen fluoride-resistant materials. Impervious graphite rupture discs fragment upon overpressure, and therefore, should not be used in conjunction with relief valves. Connections can be screwed, flanged or socket-welded for connections smaller than two inches. However, connections two inches or larger should be flanged or butt-welded. The flanges should be constructed of forged carbon steel and be rated in accordance with the associated piping system. Because operating pressures exceeding 70% of a disc's burst pressure may induce premature failure, a considerable margin should be allowed when sizing rupture discs. When it is possible to draw a vacuum on the disc, supports should be provided (23).

Instrumentation--Process instrumentation in hydrogen fluoride service often uses isolating diaphragms for corrosion protection. Pressure gauges, switches, or sensors commonly use a nickel-chromium-molybdenum alloy diaphragm, and may be filled with an inert fluid, such as chlorofluorocarbon specialty lubricants (24). Bourdon tube pressure gauges are not commonly used, but if they are would require a corrosion resistant alloy for the tube. The pressure range for both types of pressure measurement devices is commonly twice the operating pressure (29).

Similar materials considerations apply to other instrumentation such as temperature, flow, and level measurement devices. An additional consideration for all instruments is that they should be protected from external corrosion as well as direct process corrosion.

Periodic source by source fugitive emission monitoring can help identify hydrogen fluoride leaks which, if left unrepaired, might promote corrosion and increase the likelihood of a larger release. Continuous area monitoring can help detect the presence of large leaks.

The use of level gauges or weight systems can be used to monitor tank contents.

5.3.2 Plant Siting and Layout

The siting and layout of a particular hydrogen fluoride facility is a complex issue which requires careful consideration of numerous factors. These include: other processes in the area, the proximity of population centers, prevailing winds, local terrain, and potential natural external effects such as flooding. The rest of this subsection describes general considerations which might apply to siting and layout of hydrogen fluoride facilities.

Siting of facilities or individual equipment items should be done in a manner that reduces personnel exposure, both plant and public, in the event of a release. Since there are also other siting considerations, there may be trade-offs between this requirement and others in a process, some directly safety related. Siting should provide ready ingress or egress in the event of an emergency and yet also take advantage of barriers, either man made or natural which could reduce the hazards of releases. Large distances between large inventories and sensitive receptors is desirable.

Layout refers to the placement and arrangement of equipment in the process facility. All anhydrous hydrogen fluoride and aqueous hydrofluoric acid storage and handling equipment should be located away from other potentially hazardous storage and handling facilities. Such equipment is usually located in concrete enclosures or pits surrounded by curbing or walls to prevent acid spills from contaminating surrounding areas and also to serve as a boundary for the restricted acid area. Concrete containment areas are often treated with polymeric sealers to increase the containment efficiency. The drain system from the containment area should be designed to cause storm water to be routed to wastewater treating. The system should be capable of directing spilled hydrogen fluoride to a high capacity neutralization facility. Containment of hydrogen fluoride by berms of lime-containing rock has been suggested as a means of combined containment and passive neutralization. The effectiveness of these systems has not been determined.

Various techniques are available for formally assessing a plant layout and should be considered when planning high hazard facilities (23).

General layout considerations include:

- Large inventories of hydrogen fluoride should be kept away from sources of fire or explosion hazard;
- Vehicular traffic should not go too near hydrogen fluoride process or storage areas if this can be avoided;
- Where such traffic is necessary, precautions should be taken to reduce the chances for vehicular collisions with equipment, especially pipe racks carrying hydrogen fluoride across or next to roadways;
- Hydrofluoric acid piping preferably should not be located adjacent to other piping which is under high pressure or temperature, or which carries flammable materials; and
- Storage facilities should be segregated from the main process unless the hazards of pipe transport are felt to outweigh the hazard of the storage tank for site-specific cases.

Because heat increases the corrosiveness of hydrogen fluoride and causes thermal expansion of liquid hydrogen fluoride, measures should be taken to situate piping, storage vessels, and other hydrogen fluoride equipment so that they are less exposed to heat sources. Hot process piping, equipment, steam lines, and other sources of direct or radiant heat should be avoided or systems should be designed for heat induced corrosion and pressure increases. Storage should also be situated away from control rooms, offices, utilities, other hazardous storage, and laboratory areas by distances similar to those specified for flammable materials (23). Special precautions should be taken to keep hydrogen fluoride storage vessels away from potential fire or explosion sources.

In the event of an emergency, there should be multiple means of access to the facility for emergency vehicles and crews. Storage vessel shut off valves should be readily accessible. Containment for liquid storage tanks can be provided by diking. Dikes reduce evaporation while containing the liquid. It is also possible to equip a diked area to allow drainage to an underground containment sump. This sump should be vented to a scrubber system for safe discharge. A full containment system using a specially constructed building vented to a scrubber is another possible option. This type of secondary containment could be considered for large volume, liquid hydrogen fluoride storage tanks.

5.3.3 Transfer and Transport Facilities

Transfer and transport facilities where both road and rail tankers are loaded or unloaded are likely accident areas because of vehicle movement and the intermittent nature of the operations. Therefore, special attention should be given to the design of these facilities.

As mentioned in the previous section, tank car and tank truck facilities should be located away from sources of heat, fire, and explosion. Equipment in these areas should also be protected from impact by vehicles and other moving equipment. These tank vehicles should be securely moored during transfer operations; an interlocked barrier system is commonly used.

Sufficient space should be available to avoid congestion of vehicles or personnel during loading and unloading operations. Vehicles, especially trucks, should be able to move into and out of the area without reversing. High curbs around transfer areas and barriers around equipment should be provided to protect equipment from vehicle collisions.

When possible, the transfer of hydrogen fluoride should be made using fixed rigid piping. In situations which require flexible hoses or tubes, precautions must be taken to ensure sound connections. Avoiding cross contamination of chemical materials is also a key concern.

5.4 PROTECTION TECHNOLOGIES

This subsection describes two types of protection technologies for containment and neutralization. These are:

- Enclosures; and
- Scrubbers.

A presentation of more detailed information on these systems is planned in other volumes of the prevention reference manual series.

5.4.1 Enclosures

Enclosures refer to containment structures which capture any hydrogen fluoride spilled or vented from storage or process equipment, thereby preventing immediate discharge of the chemical to the environment. The enclosures contain the spilled liquid or gas until it can be transferred to other containment, discharged at a controlled rate which would not be injurious to people or the environment, or transferred at a controlled rate to scrubbers for neutralization.

The use of specially designed enclosures for hydrogen fluoride storage or process equipment does not appear to be widely practiced. The location of toxic operations in the open air has been mentioned in the literature (23), along with the opposing idea that sometimes enclosure may be appropriate. The desirability of using an enclosure depends partly on the frequency with which personnel must be involved with the equipment. A common design rationale for not having an enclosure where toxic materials are used is to prevent the accumulation of toxic concentrations within enclosed areas. However, if the issue is protecting the community from accidental releases, then total enclosure may be appropriate. Enclosures should be equipped with continuous monitoring equipment and alarms. Alarms should sound whenever lethal or flammable concentrations are detected. Enclosures for hydrogen fluoride should be equipped with adequatge fire protection.

Care must be taken when an enclosure is built around pressurized equipment. It would not be practical to design an enclosure to withstand the pressures associated with the sudden failure of a pressurized vessel. An enclosure would probably fail as a result of the pressure created from such a release and could create an additional hazard. In these situations, it may be determined that an enclosure is not appropriate. If an enclosure is built around pressurized equipment, then it should be equipped with some type of explosion protection, such as rupture plates that are designed to fail before the entire structure fails.

The type of structures that appear to be suitable for hydrogen fluoride are concrete blocks, or concrete sheet buildings or bunkers. While hydrogen fluoride would attack these structures, they would serve long enough to contain any spilled or leaked material until it could be discharged through a scrubber. An enclosure building would have a ventilation system designed to draw in air when the building was vented to a scrubber. The bottom section of the building used for stationary storage containers should be liquid tight to retain any liquid hydrogen fluoride that might be spilled. Buildings around rail tank cars used for storage do not normally lend themselves easily to effective liquid containment. However, containment could be accomplished if the floor of the building is excavated several feet below the track level while the tracks are supported at grade in the center.

While the use of enclosures for secondary containment of hydrofluoric acid spills or releases is not known to be widely used, it might be considered for areas near sensitive receptors.

5.4.2 Scrubbers

Scrubbers are a traditional method for absorbing toxic gases from process streams. These devices can be used for the control of hydrogen fluoride releases from vents and pressure relief discharges, from process equipment, or from secondary containment enclosures.

Hydrogen fluoride discharges could be contacted with an aqueous scrubbing medium in any of several types of scrubbing devices. An alkaline solution is required to achieve effective absorption because absorption rates with water alone might require unreasonably high liquid-to-gas ratios. However, water scrubbing could be used if an alkaline solution were not available. A sodium hydroxide solution would be a typical alkaline solution for an emergency scrubber.

Types of scrubbers that might be appropriate include spray towers, packed bed scrubbers, and venturis. Other types of special designs might be suitable but complex internals subject to corrosion do not seem to be advisable. Some typical absorption data for the various types of scrubbers used for hydrogen fluoride are presented in Table 5-3.

Whatever type of scrubber is selected, a complete system would include the scrubber itself, a liquid feed system, and reagent makeup equipment. If such a system is used as protection against emergency releases, consideration must be given to how it would be activated in time to respond to an emergency load. One approach used in some process facilities is to maintain a continuous circulation of scrubbing liquor through the system. For many facilities

TABLE 5-3. TYPICAL HYDROGEN FLUORIDE ABSORPTION DATA

Type of Scrubbing Equipment	Scrubbing Medium	Gas Rate (lb/hr/ft^2)	Liquid Rate (lb/hr/ft^2)	Overall Mass Transfer Coefficient, K_Ga (lb/mole/hr-ft^3-atm)	Number of Transfer Unit, N_{OG}	Efficiency (%)
Crossflow Spray	Water	2,110	72	11	0.33	28
Crossflow Spray	Water	1,880	72	12	0.38	32
Crossflow Spray	Water	2,080	103	12	0.25	22
Crossflow Spray	Water	1,830	84	15	0.62	46
Crossflow Spray	Water	1,400	92	25	1.09	66
Crossflow Spray	Lime Water	2,050	105	35	1.50	77
Counterflow Spray	Water	2,000	800	9	5.85	99+
Parallel Flow Spray	Lime Water	13,800	3,800	51	2.58	92
Counterflow Spray	Water	2,000	380	4.3	2.5	92
Venturi:	Water	76,000[a]	42,000[a]	-	2.9	94
Venturi:	Water	70,000[a]	40,000-65,000[a]	-	2.0	86
Venturi:	Water	70,000[a]	40,000-65,000[a]			
Venturi:	Water	70,000[a]	40,000-65,000[a]	-	2.3	90
Venturi	Water	70,000[a]	40,000-65,000[a]	-	3.0	95
Venturi:	Water	70,000[a]	40,000-65,000[a]	-	3.9	98
Venturi:	Water	70,000[a]	40,000-65,000[a]	-	2.3	90

[a] Based on throat cross-section.

Source: Reference 33

this would not be practical, and the scrubber system might be tied into a trip system to turn it on when it is needed. However, with this system a quantity of hydrogen fluoride would be released prior to actuation of the scrubber (i.e., starting up a blower and turning on the flow of liquid).

The scrubber system must be designed so as not to present excessive resistance to the flow of an emergency discharge. The pressure drop should be only a small fraction of the total pressure drop through the emergency discharge system. In general, at the liquid-to-gas ratios required for effective scrubbing, spray towers have the lowest, and venturis the highest pressure drops. While packed beds may have intermediate pressure drops at proper liquid-to-gas ratios, excessive ratios or plugging can increase the pressure drop substantially. However, packed beds have higher removal efficiencies than spray towers or venturis.

In addition, the scrubber system must be designed to handle the "shock wave" generated during the initial stages of the release. This is particularly important for packed bed scrubbers since there is a maximum pressure with which the gas can enter the packed section without damaging the scrubber internals.

Design of emergency scrubbers can follow standard techniques discussed in the literature, carefully taking into account the additional considerations just discussed. An example of the sizing of an emergency packed bed scrubber is presented in Table 5-4. This example provides some idea of the size of a typical emergency scrubber for various flow rates. This is an example only and should not be used as the basis for an actual system which might differ based on site specific requirements.

Another approach is the drowning tank, where the hydrogen fluoride vent is routed to the bottom of a large tank of uncirculating caustic. The drowning tank does not have the high contact efficiency of the other scrubber types, but can provide substantial capacity on demand. However, the static head associated with the drowning tank must be less than the required relief pressure in order for the system to operate.

TABLE 5-4. EXAMPLE OF PERFORMANCE CHARACTERISTICS FOR AN EMERGENCY PACKED BED SCRUBBER FOR HYDROGEN FLUORIDE

Basis: Inlet stream of 50% HF in 50% air. Constant gas flow per unit cross-sectional area of 455 scfm/ft^2.

Packing: 2 inch plastic Intalox® saddles.

Pressure Drop: 0.5 inch water column

Removal Efficiency, %	50	90
Liquid to Gas Ratio (gal/thousand scf)		
-- at flooding	140	140
-- operating	70	70
Packed Height, ft.	5.2	18.3

Column Diameter and Corresponding Gas Flow Rates for Both Removal Efficiencies

Column Diameter (ft)	Flow Rate (scfm)
0.5	90
1.0	360
2.0	1,400
6.3	14,000

5.5 MITIGATION TECHNOLOGIES

If, in spite of all precautions, a large release of anhydrous hydrogen fluoride were to occur, the first priority would be to rescue workers in the immediate vicinity of the accident and evacuate persons from downwind areas. The source of the release should be determined, and the leak should be plugged to stop the flow if this is possible. The next primary concern becomes reducing the consequences of the released chemical to the plant and the surrounding community. Reducing the consequences of an accidental release of a hazardous chemical is referred to as mitigation. Mitigation technologies include such measures as physical barriers, water sprays and fogs, and foams where applicable. The purpose of a mitigation technique is to divert, limit, or disperse the chemical that has been spilled or released to the atmosphere in order to reduce the atmospheric concentration and the area affected by the chemical. The mitigation technology chosen for a particular chemical depends on the specific properties of the chemical including its flammability, toxicity, reactivity, and those properties which determine its dispersion characteristics in the atmosphere.

If a release occurs from a pressurized liquid hydrogen fluoride storage tank above the boiling point, a quantity of liquid will immediately flash off as vapor, while the remaining liquid will be cooled to the normal boiling point of 67.1°F. Heat transfer from the air and ground will result in further vaporization of the released liquid. Since the hydrogen fluoride accidentally released from a refrigerated storage tank is already at or below its normal boiling point, a comparable quantity of vapor will not flash off, as with the pressurized release discussed above, but heat transfer from the environment will cause evaporation and the formation of a vapor cloud. It is therefore desirable to minimize the area available for heat transfer to a liquid spill which in turn will minimize the rate of evaporation. Mitigation technologies which are used to reduce the rate of evaporation of a released liquified gas include secondary containment systems such as impounding basins, dikes, and enclosures.

A post release mitigation effort requires that the source of the release be accessible to trained plant personnel. Therefore, the availability of adequate personnel protection is essential. Personnel protection will typically include such items as portable breathing air and chemically resistant protective clothing.

5.5.1 Secondary Containment Systems

Specific types of secondary containment systems include excavated basins, natural basins, earth, steel, or concrete dikes, and high impounding walls. The type of containment system best suited for a particular storage tank or process unit will depend on the risk associated with an accidental release from that location. The inventory of hydrogen fluoride and its proximity to other portions of the plant and to the community should be considered when selecting a secondary containment system. The secondary containment system should have the ability to contain spills with a minimum of damage to the facility and its surroundings and with minimum potential for escalation of the event.

Secondary containment systems for hydrogen fluoride storage facilities commonly consist of one of the following:

- An adequate drainage system underlying the storage vessels which terminates in a lime containing neutralization basin having a capacity as large as the largest tank served;

- A diked area with a capacity as large as the largest tank served.

These measures are designed to prevent the accidental discharge of liquid hydrogen fluoride from spreading to uncontrolled areas.

The most common type of containment system is a low wall dike surrounding one or more storage tanks. Generally, no more than three tanks are enclosed within one diked area to reduce risk. Dike heights usually range from three to twelve feet depending on the area available to achieve the required volumetric capacity. The dike walls should be liquid tight and able to withstand the hydrostatic pressure and temperature of a spill. Low wall dikes may be constructed of steel, concrete or earth. If earthen dikes are used, the dike wall must be constructed and maintained to prevent leakage through the dike. Piping should be routed over dike walls, and penetrations through the walls should be avoided if possible. Vapor fences may be situated on top of the dikes to provide additional vapor storage capacity. If there is more than one tank in the diked area, the tanks should be situated on berms above the maximum liquid level attainable in the impoundment.

A low wall dike can effectively contain the liquid portion of an accidental release and keep the liquid from entering uncontrolled areas. By preventing the liquid from spreading, the low wall dike can reduce the surface area of the spill. Reducing the surface area will reduce the rate of evaporation. The low wall dike will partially protect the spill from wind; this can reduce the rate of evaporation. A dike with a vapor fence will provide extra protection from wind and will be even more effective at reducing the rate of evaporation.

A dike also creates the potential for hydrogen fluoride and trapped water to mix in the dike, which may accelerate the rate of evaporation and form highly corrosive hydrofluoric acid. If materials that would react violently with hydrogen fluoride are stored within the same diked area then the dike will increase the potential for mixing the materials in the event of a simultaneous leak. A dike also limits access to the tank during a spill.

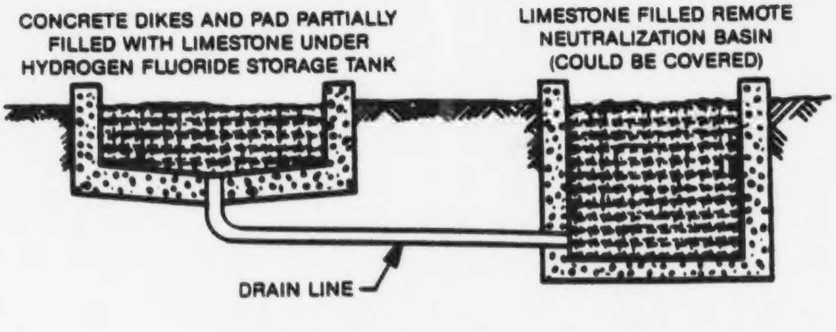
A neutralization basin is well suited to storage systems where more than one tank is served and a relatively large site is available. The flow from a hydrogen fluoride spill is directed to the basin by dikes and channels under the storage tanks which are designed to minimize exposure of the liquid to other tanks and surrounding facilities. In the basin, the hydrogen fluoride is mixed with lime to form an insoluble fluoride sludge which can be hauled away for disposal (34). The lime could be stored in the basin either as a premixed slurry or as solid limestone. Figure 5-2 illustrates two potential layouts for a remote neutralization basin. Because of hydrogen fluoride's high vapor pressure, the trenches that lead to the neutralization basin should be covered to reduce the rate of evaporation. Additionally, the neutralization basin should be located near the tank area to minimize the amount of hydrogen fluoride that evaporates as it travels to the basin.

This type of system has several advantages. The spilled liquid is removed from the immediate tank area. This allows access to the tank during the spill and reduces the probability that the spilled liquid will damage the tank, piping, electrical equipment, pumps or other equipment. In addition, a lime containing basin will immediately neutralize the hydrogen fluoride and prevent its release to the atmosphere.

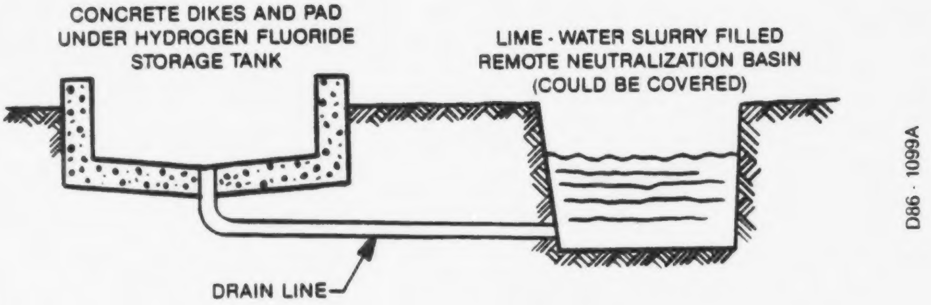
A limitation of a neutralization basin is that they do not completely reduce the impact of a gaseous release. Additionally, the reaction of lime with hydrogen fluoride is exothermic. The heat generated by the neutralization could result in an increase in the rate of evaporation of the liquid.

An alternative to a lime filled basin would be to allow the spilled liquid to flow into a covered, empty basin. The vapor from the basin could be directed to a scrubbing system. The advantage of this system is that the scrubber could be sized to accommodate the vapor generated from the spilled liquid. The disadvantages are the same as those mentioned in Section 5.4.2 where scrubbers as a protection technology are discussed.

Although few authorities for hydrogen fluoride facilities require them, high wall impoundments may be a good secondary containment choice for selected systems. Circumstances which may warrant their use include limited storage


CONCRETE DIKES AND PAD PARTIALLY FILLED WITH LIMESTONE UNDER HYDROGEN FLUORIDE STORAGE TANK
LIMESTONE FILLED REMOTE NEUTRALIZATION BASIN (COULD BE COVERED)
DRAIN LINE

LIMESTONE NEUTRALIZATION BASIN


CONCRETE DIKES AND PAD UNDER HYDROGEN FLUORIDE STORAGE TANK
LIME - WATER SLURRY FILLED REMOTE NEUTRALIZATION BASIN (COULD BE COVERED)
DRAIN LINE
D86 - 1099A

LIME WATER NEUTRALIZATION SYSTEM

Figure 5-2. Potential layouts for a neutralization basin system.

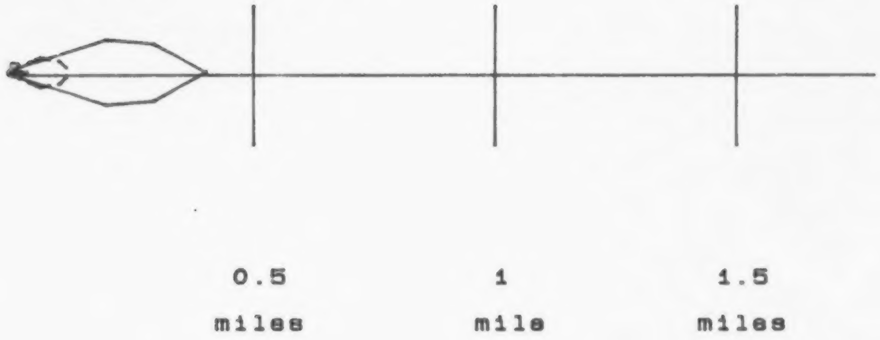
Source: Adapted from Reference 34.

site area, the need to minimize vapor generation rates, and/or the tank must be protected from external hazards. Maximum vapor generation rates will generally be lower for a high wall impoundment than for low wall dikes or remote impoundments because of the reduced surface contact area. These rates can be further reduced with the use of insulation on the wall and floor in the annular space. High impounding walls may be constructed of low temperature steel, reinforced concrete, or prestressed concrete. A weather shield may be provided between the tank and wall with the annular space remaining open to the atmosphere. The available area surrounding the storage tank will dictate the minimum height of the wall. For high wall impoundments, the walls may be designed with a volumetric capacity greater than that of the tank to provide vapor containment. Increasing the height of the wall also raises the elevation of any released vapor.

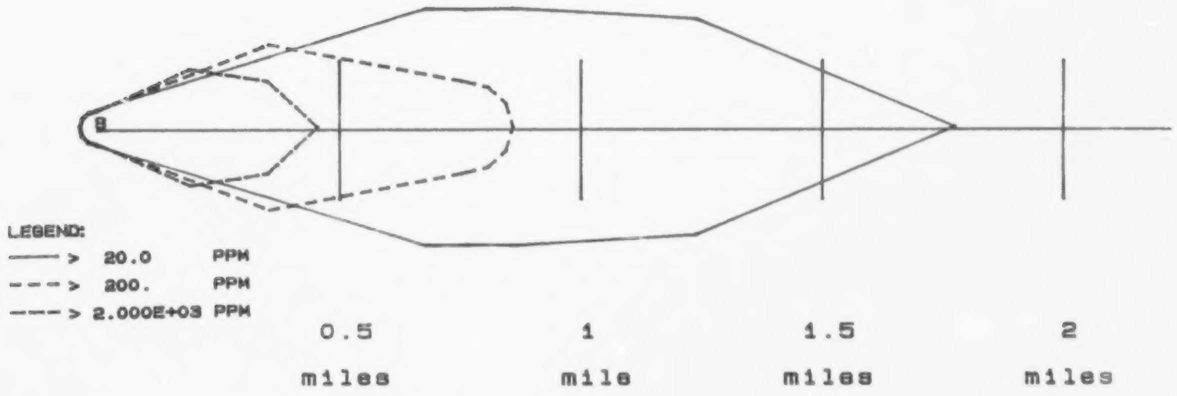
One disadvantage of these dikes is that the high walls around a tank may hinder routine external observation. Furthermore, the closer the wall is to the tank, the more difficult it becomes to access the tank for inspection and maintenance. As with low wall dikes, piping should be routed over the wall if possible. The closeness of the wall to the tank may necessitate placement of the pump outside of the wall, in which case the outlet (suction) line will have to pass through the wall. In such a situation, a low dike encompassing the pipe penetration and pump may be provided, or a low dike may be placed around the entire wall.

An example of the effect of diking as predicted by one vapor dispersion model is shown in Figure 5-3 (35). With diking the predicted maximum IDLH exposure occurs at a distance of 2,100 feet downwind from the release source at 3 minutes after release. Without diking the predicted maximum IDLH exposure occurs at a distance of 9,400 feet at 13 minutes after exposure.

One further type of secondary containment system is one which is structurally integrated with the primary system and forms a vapor tight enclosure around the primary container. Many types of arrangements are possible. A


0.5
miles
1
mile
1.5
miles

Release from a tank surrounded by a 25 ft. diameter dike.
Elapsed Time: 3 minutes


LEGEND:
——— > 20.0 PPM
– – – > 200. PPM
—– – > 2.000E+03 PPM
0.5
miles
1
mile
1.5
miles
2
miles

Release from a tank with no dike.
Elapsed Time: 13 minutes

Common Release Conditions:
Storage Temperature = 40°F
Storage Pressure = 14.7 psia
Ambient Temperature = 85°F

Wind Speed = 10 mph
Atmospheric Stability Class = C
Quantity Released = 5000 gallons through a 2-inch hole

Figure 5-3. Computer model simulation showing the effect of diking on the vapor cloud generated from a release of refrigerated hydrogen fluoride.

double walled tank is an example of such an enclosure. These systems may be considered where protection of the primary container and containment of vapor for events not involving foundation or wall penetration failure are of greatest concern. Drawbacks of an integrated system are the greater complexity of the structure, the difficulty of access to certain components, and the fact that complete vapor containment cannot be guaranteed for all potential events.

Provision should be made for drainage of rainwater from diked areas. This will involve the use of sumps and separate drainage pumps, since direct drainage to stormwater sewers would presumably allow any spilled hydrogen fluoride to follow the same route. Alternately, a sloped rain hood may be used over the diked area which could also serve to direct the rising vapors to a single release point (36). The ground within the enclosure should be graded to cause the spilled liquid to accumulate at one side or in one corner. This will help to minimize the area of ground to which the liquid is exposed and from which it may gain heat. In areas where it is critical to minimize vapor generation, surface insulation may be used in the diked area to further reduce heat transfer from the environment to the spilled liquid. The floor of an impoundment should be sealed with a clay blanket to prevent the hydrogen fluoride from seeping into the ground; percolation into the ground causes the ground to cool more quickly, increasing the vapor generation rate. Absorption of the hydrogen fluoride into water in the soil would also release additional heat.

5.5.2 Flotation Devices and Foams

Other possible means of reducing the surface area of spilled hazardous chemicals include placing impermeable flotation devices on the surface, dilution with water, and applying water-based foam. However, where hydrogen fluoride releases are concerned, neither of these are satisfactory.

Placing an impermeable flotation device over a spilled chemical is a direct approach for containing toxic vapors with nearly 100 percent efficiency. However, being able to use such devices requires acquisition in advance of a spill and storage until needed. In addition, deployment may be difficult in all but small spills.

Although such devices are potentially effective, no systems are currently available for use in mitigating hydrogen fluoride spills. The primary deterent to their use is the cost associated with material and disposal equipment. Such a system would require the dispersal of a minimum of 280 particles per square foot of spill material (37). Based on 1986 prices, material costs would be approximately $100 per square foot, with dispersal equipment costs running 100 times the cost (37).

The use of foams in vapor hazard control has been demonstrated for a broad range of volatile chemicals. However, no foam systems are currently available for use with hydrogen fluoride. Results of a laboratory test program conducted by the Mine Safety Appliance (MSA) Research Corporation (37) to evaluate the applicability and effectiveness of various foams for various hazardous chemicals including hydrogen fluoride showed that because of the extremely high heat of solution, hydrogen fluoride boils and fumes violently upon application of foam.

Finally, the dilution of a hydrogen fluoride spill with water will result in highly corrosive hydrofluoric acid. In addition, because of the high heat of solution, the addition of pure water results in violent boil-off of hydrogen fluoride and a dispersal of corrosive acid. Thus, water should not be used on a pool of hydrogen fluoride.

One alternative for hydrogen fluoride spills is to spread soda ash on the spill or use a strong soda ash solution to act as a neutralizing agent and prevent the release of toxic hydrogen fluoride vapors.

Another alternative for retarding evaporation of liquid hydrogen fluoride is to use a paraffin-base oil. A test program using several agents including an oil with a viscosity of 675 Saybolt seconds at 100°F was conducted by Union Carbide Corporation (39). The results showed that this type of oil spread over the surface and effectively sealed the vapors without being destroyed. Any oil used must have a high enough flash point to prevent a secondary fire hazard from resulting.

5.5.3 Mitigation Techniques for Hydrogen Fluoride Vapor

The extent to which the escaped hydrogen fluoride vapor can be removed or dispersed in a timely manner will be a function of the quantity of vapor released, the ambient conditions, and the physical characteristics of the vapor cloud. The behavior and characteristics of the hydrogen fluoride cloud will be dependent on a number of factors. These include the physical state of the hydrogen fluoride before its release, the location of the release, and the atmospheric and environmental conditions. Many possibilities exist concerning the shape and motion of the vapor cloud, and a number of predictive models of dispersion have been developed. As a result of the higher specific gravity of pure hydrogen fluoride, large accidental releases of hydrogen fluoride will often result in the formation of hydrogen fluoride-air mixtures which are denser than the surrounding atmosphere. This type of vapor cloud is especially hazardous, because it will spread laterally and remain close to the ground. At this writing, research data from tests on hydrogen fluoride releases is being analyzed (40). When these results are published much more will be known on the behavior of hydrogen fluoride under actual release conditions.

One possible means of dispersing as well as removing toxic vapor from the air is with the use of water sprays or fogs. However, dilution of hydrogen fluoride with water results in the formation of highly corrosive hydrofluoric acid and presents an additional health hazard to plant personnel as well as corrosion problems for machinery and equipment. In addition, to be effective, an impractically large volume of water might have to be used, although it may be beneficial in controlling relatively small releases where principal hazard is to plant personnel (41). An alternative is to use a mild aqueous alkaline spray system such as an ammonia-injected water spray system which would act as a neutralizing agent for the acid. Although such systems do not appear to be widely used for the mitigation of hydrogen fluoride vapors, they are used for other toxic chemicals of similar nature (42).

The spray medium is typically applied to the vapor cloud by means of hand-held hoses and/or stationary water-spray barriers. Important factors relating to the effectiveness of spray systems are the distance of the nozzles from the point of release, the fog pattern, nozzle flow rate, pressure, and nozzle rotation. If spray systems are used to mitigate hydrogen fluoride vapors from a diked area containing spilled liquid hydrogen fluoride, great care must be taken not to direct water into the liquid hydrogen fluoride itself.

Several techniques have also been developed to effectively disperse toxic vapor resulting from major leaks in piping and equipment. One such technique has been developed by Beresford (43). Although such a system has not been used for the mitigation of hydrogen fluoride vapor, they have been effectively used for other toxic chemicals of similar nature (43).

The method consists of coarse water sprays discharging upwards from flat fan sprays and wide-angled spray monitors arranged so that a vent or chimney effect is created to completely surround the toxic vapor. Results have shown that the high velocity water droplets induce large volumes of air at ground level as the water discharges upwards (43). The air is caused to move upwards through the chimney formed by the sprays. As the air moves over the ground, the heavier than air toxic gas is diluted and pushed up and out of the top of the chimney where it dispenses safely. Design details are presented in Beresford (43). Both types of spray methods are incorporated into the design since the flat-fan sprays effectively stop the lateral spread of vapor and the monitors provide the required air movement for dilution and dispersal.

Another means of dispersing a vapor cloud is with the use of large fans or blowers which would direct the vapor away from populated or other sensitive areas (44). However, this method would only be feasible in very calm weather and in sheltered areas; it would not be effective in any wind and would be difficult to control if the release occupies a large open area. A large, mechanical blower would also be required which lowers the reliability of this mitigation technique compared to water fogs and sprays.

In general, techniques used to disperse or control vapor emissions should emphasize simplicity and reliability. In addition to the mitigation techniques discussed above, physical barriers such as buildings and rows of trees may help to contain the vapor cloud and control its movement. Additional discussions concerning mitigation technologies will be found in a manual on control technologies, part of this manual series.

5.6 OPERATION AND MAINTENANCE PRACTICES

Quality hardware, contained mechanical equipment, and protective devices all increase plant safety; however, they must be supported by the safety policies of management and by constraints on their operation and maintenance. This section describes how management policy and training, operation, and maintenance procedures relate to the prevention of accidental chlorine releases. Within the hydrogen fluoride industry, these procedures and practices vary widely because of differences in the size and nature of the processes and because any determination of their adequacy is inherently subjective. For this reason, the following subsections focus primarily on fundamental principles and do not attempt to define specific policies and procedures.

5.6.1 Management Policy

Management is a key factor in the control of industrial hazards and the prevention of accidental releases. Management establishes the broad policies and procedures which influence the implementation and execution of specific hazard control measures. It is important that these management policies and procedures be designed to match the level of risk in the facilities where they will be used. Most organizations have a formal safety policy. Many make policy statements to the effect that safety must rank equally with other company functions such as production and sales. The effectiveness of any safety program, however, is determined by a company's commitment to it, as demonstrated throughout the management structure. Specific goals must be derived from the safety policy and supported by all levels of management. Safety and loss prevention should be an explicit management objective. Ideally, management should establish the specific safety performance measures, provide incentives for attaining safety goals, and commit company resources to safety and hazard control. The advantages of an explicit policy are that it sets the standard by which existing programs can be judged, and it provides evidence that safety is viewed as a significant factor in company operations.

In the context of accident prevention, management is responsible for (23,45):

- Ensuring worker competency,
- Developing and enforcing standard operating procedures,
- Adequate documentation of policy and procedures,
- Communicating and promoting feedback regarding safety issues,
- Identification, assessment, and control of hazards, and
- Regular plant audits and provisions for independent checks.

Additional discussion on the responsibilities of management will be found in a manual on control technologies, part of this manual series.

5.6.2 Operator Training

The performance of operating personnel is also a key factor in the prevention of accidental hydrogen fluoride releases. Many case studies documenting industrial incidents note the contribution of human error to accidental releases (23). Release incidents may be caused by using improper routine operating procedures, by insufficient knowledge of process variables and equipment, by lack of knowledge about emergency or upset procedures, by failure to recognize critical situations, and in some cases by direct physical mistake (e.g., turning the wrong valve). A comprehensive operator training program can decrease the potential for accidents resulting from such causes.

Operator training can include a wide range of activities and a broad spectrum of information. Training, however, is distinguished from education in that it is specific to particular tasks. While general education is important and beneficial, it is not a substitute for specific training. The content of a specific training program depends on the type of industry, the nature of the processes used, the operational skills required, the characteristics of the plant management system, and tradition.

Some general characteristics of quality industrial training programs include:

- Establishment of good working relations between management and personnel,
- Definition of trainer responsibilities and training program goals,

- Use of documentation, classroom instruction, and field training (in some cases supplemented with simulator training),

- Inclusion of procedures for normal startup and shutdown, routine operations, and upsets, emergencies, and accidental releases, and

- Frequent supplemental training and the use of up-to-date training materials.

In many instances training is carried out jointly by plant managers and a training staff selected by management. In others, management is solely responsible for maintaining training programs. In either case, responsibilities should be explicitly designated to ensure that the quality and quantity of training provided is adequate. Training requirements and practices can be expected to differ between small and large companies, partly because of resource needs and availability, and partly because of differences in employee turnover.

A list of the aspects typically involved in the training of process operators for routine process operations is presented in Table 5-5.

Emergency training includes topics such as:

- Recognition of alarm signals,

- Performance of specific functions (e.g., shutdown switches),

- Use of specific equipment,

- Actions to be taken on instruction to evacuate,

TABLE 5-5. ASPECTS OF TRAINING PROGRAMS FOR ROUTINE PROCESS OPERATIONS

- Process goals, economics, constraints, and priorities
- Process flow diagrams
- Unit Operations
- Process reactions, thermal effects
- Control systems
- Process materials quality, yields
- Process effluents and wastes
- Plant equipment and instrumentation
- Equipment identification
- Equipment manipulation
- Operating procedures
- Equipment maintenance and cleaning
- Use of tools
- Permit systems
- Equipment failure, services failure
- Fault administration
  - Alarm monitoring
  - Fault diagnosis
  - Malfunction detection
- Communications, recordkeeping, reporting

Source: Reference 23

- Fire fighting, and
- Rehearsal of emergency situations.

Aspects specifically addressed in safety training include (23,43):

- Hazard recognition and communication,
- Actions to be taken in particular situations,
- Available safety equipment and locations,
- When and how to use safety equipment,
- Use and familiarity with documentation such as,
  - plant design and operating manuals,
  - company safety rules and procedures,
  - procedures relevant to fire, explosion, accident, and health hazards,
  - chemical property and handling information, and
- First aid and CPR.

Although emergency and safety programs typically focus on incidents such as fires, explosions, and personnel safety, it is important that prevention of accidental chemical releases and release responses be addressed as part of these programs.

Much of the type of training discussed above is also important for management personnel. Safety training gives management the perspective necessary to formulate good policies and procedures, and to make changes that will improve the quality of plant safety programs. Lees suggests that training programs applied to managers include or define (23):

- Overview of technical aspects of safety and loss prevention approach,

- Company systems and procedures,

- Division of labor between safety personnel and managers in with respect to training, and

- Familiarity with documented materials used by workers.

5.6.3 Maintenance and Modification Practices

Plant maintenance is necessary to ensure the structural integrity of chemical processing equipment; modifications are often necessary to allow more effective production. However, since these activities are also a primary source of accidental release incidents, proper maintenance and modification practices are an important part of accidental release prevention. Use of a formal system of controls is perhaps the most effective way of ensuring that maintenance and modification are conducted safely. In many cases, control systems have had a marked effect on the level of failures experienced (23).

Permit systems and up-to-date maintenance procedures minimize the potential for accidents during maintenance operations. Permit-to-work systems control maintenance activities by specifying the work to be done, defining individual responsibilities, eliminating or protecting against hazards, and ensuring that appropriate inspection and testing procedures are followed.

Maintenance permits originate with the operating staff. Permits may be issued in one or two stages. In one-stage systems, the operations supervisor issues permits to the maintenance supervisor, who is then responsible for his staff. Two-stage systems involves a second permit issued by the maintenance supervisor to his workforce (23).

Another form of maintenance control is the maintenance information system. Ideally, these systems should log the entire maintenance history of equipment, including preventative maintenance, inspection and testing, routine servicing, and breakdown or failure maintenance. This type of system is also used to track incidents caused by factors such as human error, leaks, and fires, including identification and quantification of failures responsible for hazardous conditions, failures responsible for downtime, and failures responsible for direct repair costs.

Accidental releases are frequently the result of some aspect of plant modification. Accidents result when equipment integrity and operation are not properly assessed following modification, or when modifications are made without updating corresponding operation and maintenance instructions. In these situations, it is important that careful assessment of the modification results has a priority equal to that of getting the plant on-line.

For effective modification control, there must be established procedures for authorization, work activities, inspection, and assessment, complete documentation of changes, including the updating of manuals, and additional training to familiarize operators with new equipment and procedures (23,45).

Formal procedures and checks on maintenance and modification practices must be established to ensure that such practices enhance rather than adversely affect plant safety. As with other plant practices, procedure development and complete documentation are necessary. However, training, attitude, and the degree to which the procedures are followed also significantly influence plant safety and release prevention.

The use and availability of clearly defined procedures collected in maintenance and operating manuals is crucial for the prevention of accidental releases. Well-written instructions should give enough information about a process that the worker with hands-on responsibility for operating or maintaining the process can do so safely, effectively, and economically. These instructions not only document the path to the desired results, but also are the basis for most industrial training programs (46,47). In the chemical industry, operating and maintenance manuals vary in content and detail. To some extent, this variation is a function of process type and complexity; however, in many cases it is a function of management policy. Because of their importance to the safe operation of a chemical process, these manuals must be as clear, straightforward, and complete as possible. In addition, standard procedures should be developed and documented before plant startup, and appropriate revisions should be made throughout plant operations.

Operation and maintenance may be combined or documented separately. Procedures should include startup, shutdown, hazard identification, upset conditions, emergency situations, inspection and testing, and modifications (23). Several authors think industrial plant operating manuals should include (23,45,46,47):

- Process descriptions,
- A comprehensive safety and occupational health section,
- Information regarding environmental controls,
- Detailed operating instructions, including startup and shutdown procedures,
- Upset and emergency procedures,
- Sampling instructions,
- Operating documents (e.g., logs, standard calculations),
- Procedures related to hazard identification,

- Information regarding safety equipment,
- Descriptions of job responsibilities, and
- Reference materials.

Plant maintenance manuals typically contain procedures not only for routine maintenance, but also for inspection and testing, preventive maintenance, and plant or process modifications. These procedures include specific items such as codes and supporting documentation for maintenance and modifications (e.g., permits-to-work, clearance certificates), equipment identification and location guides, inspection and lubrication schedules, information on lubricants, gaskets, valve packings and seals, maintenance stock requirements, standard repair times, equipment turnaround schedules, and specific inspection codes (e.g., for vessels and pressure systems) (23). Full documentation of the maintenance required for protective devices is a particularly important aspect of formal maintenance systems.

The preparation of operating and maintenance manuals, their availability, and the familiarity of workers with their contents are all important to safe plant operations. The objective, however, is to maintain this safe practice throughout the life of the plant. Therefore, as processes and conditions are modified, documented procedures must also be modified.

5.7 CONTROL EFFECTIVENESS

It is difficult to quantify the control effectiveness of preventive and protective measures to reduce the probability and magnitude of accidental releases. Preventive measures, which may involve numerous combinations of process design, equipment design, and operational measures, are especially difficult to quantify because they reduce a probability rather than a physical quantity of a chemical release. Protective measures are more analogous to traditional pollution control technologies. Thus, they may be easier to quantify in terms of their efficiency in reducing a quantity of chemical that could be released.

Preventive measures reduce the probability of an accidental release by increasing the reliability of both process systems operations and the equipment. Control effectiveness can thus be expressed for both the qualitative improvements and the quantitative improvements through probabilities. Table 5-6 summarizes what appear to be some of the major design, equipment, and operational measures applicable to the primary hazards identified for the hydrogen fluoride applications in the United States. The items listed in Table 5-6 are for illustration only and do not necessarily represent satisfactory control options for all cases. These control options appear to reduce the risk associated with an accidental release when viewed from a broad perspective. However, there are undoubtedly specific cases where these control options will not be appropriate. Each case must be evaluated individually. A presentation of more information about reliability in terms of probabilities is planned in other volumes of the prevention reference manual series.

5.8 ILLUSTRATIVE COST ESTIMATES FOR CONTROLS

This section presents cost estimates for different levels of control and for specific release prevention and protection measures for hydrogen fluoride storage and process facilities that might be found in the United States.

5.8.1 Prevention and Protection Measures

Preventive measures reduce the probability of an accidental release from a process or storage facility by increasing the reliability of both process systems operations and equipment. Along with an increase in the reliability of a system is an increase in the capital and annual costs associated with incorporating prevention and protection measures into a system. Table 5-7 presents costs for some of the major design, equipment, and operational

TABLE 5-6. EXAMPLES OF MAJOR PREVENTION AND PROTECTION MEASURES FOR HYDROGEN FLUORIDE RELEASES

Hazard Area	Prevention/Protection
Water contamination in hydrocarbon feeds to alkylation	Continuous moisture monitoring; Backflow prevention
Sulfur contamination in hydrocarbon feeds to alkylation	Continuous sulfur monitoring
Hydrogen fluoride flow control	Redundant flow control loops; Minimal overdesign of feed systems
Temperature sensing and cooling medium flow control	Redundant temperature sensors; Interlock flow switch to shut off HF feed on loss of cooling, with relief venting to emergency scrubber system
Temperature sensing and heating medium flow control	Redundant temperature sensors; Interlock flow switch to shut off HF feed on loss of heating, with relief venting to emergency scrubber system
Overpressure	Redundant pressure relief; adequate size; discharge not restricted
Mixing in alkylation reactors	Interlock HF and olefin feed shutoff with loss of mixing
Corrosion	Increased monitoring with more frequent inspections; use of pH sensing on cooling water and steam condensate loops; use of corrosion coupons[a]; visual inspections; non-destructive testing

(Continued)

TABLE 5-6 (Continued)

Hazard Area	Prevention/Protection
Reactor and reboiler temperatures	Redundant temperature sensing and alarms
Overfilling	Redundant independent level sensing, alarms and interlocks; training of operators
Atmosphere releases from relief discharges	Emergency vent scrubber system
Storage tank or line rupture	Enclosure vented to emergency scrubber system; diking; foams; dilution; neutralization; water sprays

[a] A piece of metal of known composition which is used to monitor corrosion rates by allowing it to reside in the corrosive environment and measuring the amount of corrosion as a function of time.

TABLE 5-7. ESTIMATED TYPICAL COSTS OF MAJOR PREVENTION AND PROTECTION MEASURES FOR HYDROGEN FLUORIDE RELEASES[a]

Prevention/Protection Measure	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
Continuous moisture monitoring	7,500-10,000	900-1,300
Flow control loop	4,000-6,000	500-750
Temperature sensor	250-400	30-50
Pressure relief		
- relief valve	1,000-2,000	120-250
- rupture disk	1,000-1,200	120-150
Interlock system for flow shut-off	1,500-2,000	175-250
pH monitoring of cooling water	7,500-10,000	900-1,300
Alarm system	250-500	30-75
Level sensor		
- liquid level gauge	1,500-2,000	175-250
- load cell	10,000-15,000	1,300-1,900
Diking (based on a 10,000 gal. tank)		
- 3 ft. high	1,200-1,500	150-175
- top of tank height, 10 ft.	7,000-7,500	850-900
Increased corrosion inspection[b]		200-400

[a] Based on a 10,000 gallon fixed hydrogen fluoride storage tank system and a 147,000 gallon/day alkylation reactor system.

[b] Based on 10-20 hours @ $20/hour.

measures applicable to the primary hazards identified in Table 5-6 for the hydrogen fluoride applications in the United States.

5.8.2 Levels of Control

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices as they apply to the design, construction, and operation of facilities where hazardous chemicals are used and stored. Inherent in determining the degree to which these practices are carried out is their costs. At a minimum, equipment and procedures should be in accordance with applicable codes, standards, and regulations. However, additional measures can be taken to provide extra protection against an accidental release.

The levels of control concept provides a means of assigning costs to increased levels of prevention and protection. The minimum level is referred to as the "Baseline" system. This system consists of the elements required for normal safe operation and basic prevention of an accidental release of hazardous material.

The second level of control is "Level 1". "Level 1" includes the baseline system with added modifications such as improved materials of construction, additional controls, and generally more extensive release prevention measures. The costs associated with this level are higher than the baseline system costs.

The third level of control is "Level 2". This system incorporates both the "Baseline" and "Level 1" systems with additional modifications designed specifically for the prevention of an accidental release such as alarm and interlock systems. The extra accidental release prevention measures incorporated into "Level 2" are reflected in its cost, which is much higher than that of the baseline system.

When comparing the costs of the various levels of control, it is important to realize that higher costs do not necessarily imply improved safety. The measures applied must be applied correctly. Inappropriate modifications or add-ons may not make a system safer. Each added control option increases the complexity of a system. In some cases, the hazards associated with the increased complexity may outweigh the benefits derived from the particular control option. Proper design and construction along with proper operational practices are needed to assure safe operation.

These estimates are for illustrative purposes only. It is doubtful that any specific installation would find all of the control options listed in these tables appropriate for their purposes. An actual system is likely to incorporate some items from each of the levels of control and also some control options not listed here. The purpose of these estimates is to illustrate the relationship between cost and control, and is not to provide an equipment check list.

Two sets of cost estimates were prepared; one for a 42 ton fixed hydrogen fluoride storage tank system with 10,000 gal capacity and the other for a hydrogen fluoride alkylation reactor system for a 147,000 gal/day alkylate capacity plant. These systems are representative of storage and process facilities that might be found in the United States.

5.8.3 Cost Summaries

Table 5-8 presents a summary of the total capital and annual costs for each of the three levels of control for the hydrogen fluoride storage system and the hydrogen fluoride alkylation reactor system. The costs presented correspond to the systems described in Table 5-9 and Table 5-10. Each of the level costs include the cost of the basic system plus any added controls. Specific cost information and breakdown for each level of control for both the storage and process facilities are presented in Table 5-11 through 5-16.

TABLE 5-8. SUMMARY COST ESTIMATES OF POTENTIAL LEVELS OF CONTROLS FOR HYDROGEN FLUORIDE STORAGE TANK AND ALKYLATION REACTOR

System	Level of Control	Total Capital Cost (1986 $)	Total Annual Cost (1986 $/yr)
HF Storage Tank; 42 ton	Baseline	147,000	18,000
Fixed HF Tank with 10,000 gal	Level No. 1	471,000	56,000
Capacity	Level No. 2	1,312,000	154,000
HF Alkylation Reactor at Typical Operating	Baseline	2,425,000	332,000
Conditions of 75-100°F and 80-115 psig with a	Level No. 1	4,172,000	544,000
147,000 gal/day alkylate capacity	Level No. 2	4,453,000	579,000

TABLE 5-9: EXAMPLE OF LEVELS OF CONTROL FOR HYDROGEN FLUORIDE STORAGE TANK[a]

Process: 42 ton fixed hydrogen fluoride storage tank
10,000 gal

Controls	Baseline	Level No. 1	Level No. 2
Flow:	Single check-valve on tank-process feed line.	Add second check valve.	Add a reduced-pressure device[b] with internal air gap and relief vent to containment tank or scrubber.
Temperature:	None	None	Add temperature indicator.
Pressure:	Single pressure relief valve, vent to atmosphere.	Add second relief valve. Vent to limited scrubber. Provide local pressure indicator.	Add rupture disks under relief valves. Provide local pressure indication on space between disk and valve.
Quantity:	Local level indicator.	Add independent remote level indicator.	Add level alarm. Add high-low level interlock shut-off for both inlet and outlet lines.
Location:	Away from traffic, and flammables, and other hazardous processes.	Away from traffic, flammables, and other hazardous processes.	Away from traffic, flammables, and other hazardous processes.
Materials of Construction:	Carbon steel.	Carbon steel with increased corrosion allowances. 1/8 inch	Monel®.
Vessel:	Tank pressure specification 150 psig.	Tank pressure specification psig[c].	Tank pressure specification 375 psig[c].

(continued)

TABLE 5-9 (Continued)

Process: 42 ton fixed hydrogen fluoride storage tank
10,000 gal

Controls	Baseline	Level No. 1	Level No. 2
Piping:	Sch. 80 carbon steel.	Sch. 80 Saran®-lined carbon steel.	Sch 80 Monel®.
Process Machinery:	Centrifugal pump, carbon steel, stuffing box.	Centrifugal pump, Monel® construction, double capacity mechanical seal.	Magnetically-coupled centrifugal pump, Monel® construction.
Enclosures:	None	Steel building.	Concrete building.
Diking:	None	3 ft high.	Top of tank height, 10 ft.
Scrubbers:	None	Water scrubber.	Alkaline scrubber.
Mitigation:	None	Water sprays.	Alkaline water sprays and barriers.

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[a] The examples in this table are appropriate for many, but not all applications. This is only an exemplary system. Design must be suited to fit the service.

[b] A reduced pressure device is a modified double check valve.

[c] Note that tank pressure specification will be a function of maximum operating pressure. These values are chosen only as representative examples.

TABLE 5-10: EXAMPLE OF LEVELS OF CONTROL FOR HYDROGEN FLUORIDE ALKYLATION REACTOR[a]

Process: HF alkylation

Typical Operating Conditions: - Temperature: 75-100°F

- Pressure: 80-115 psig

Controls	Baseline	Level No. 1	Level No. 2
Process:	Dryers on feed lines.	Improved reactor design.	Use of interlock systems.
Temperature:	Provide local temperature control.	Add redundant temperature sensors and alarms. Add remote temperature indicator.	Add temperature switch and back-up cooling system.
Pressure:	Provide local pressure control. Single pressure relief valve. Vent to atmosphere.	Add redundant pressure sensors. Add second relief valve. Vent to limited scrubber. Add remote pressure indicator.	Add rupture disks under relief valves and provide local and remote pressure indicator on space between disk and valve.
Flow:	Provide local flow control on HF feed and cooling medium to reactor.	Add redundant flow control loops.	Add interlock flow switch to shut off HF feed on loss of cooling medium.
Quantity:	None.	None.	None.
Mixing:	Provide adequate mixing.	Add agitation detection system.	Interlock HF and olefin feed shut off with loss of mixing.
Corrosion:	Visual inspection and pH monitoring of cooling medium.	Increased monitoring with increased inspections.	Add pH sensing on reactor cooling medium. Add corrosion coupons.

(Continued)

TABLE 5-10 (Continued)

Process: HF alkylation

Typical Operating Conditions: - Temperature: 75-100°F
- Pressure: 80-115 psig

Controls	Baseline	Level No. 1	Level No. 2
Composition:	Dryers on feed lines.	Occasional moisture monitoring of feed.	Continuous moisture monitoring of feed.
Material of Construction:	Carbon-steel	Carbon steel with added corrosion allowance.	Monel®.
Vessel:	Pressure specification: 150 psig.	Pressure specification: 200 psig.	Pressure specification: 200 psig.
Piping:	Sch 80 carbon steel.	Sch 80 Saran® lined carbon steel.	Sch 80 Monel®.
Process Machinery:	Centrifugal pump, carbon steel construction, stuffing box.	Centrifugal pump, Monel® construction, double capacity mechanical seal.	Magnetically-coupled centrifugal pump, Monel® construction.
Protective Barrier:	None.	Curbing around reactor/settler.	3 ft high retaining wall.
Enclosures:	None.	Steel building.	Concrete building.
Scrubbers:	None.	Water scrubbers.	Alkaline scrubbers.
Mitigation:	None.	Water sprays.	Alkaline water sprays.

[a] The examples in this table are appropriate for many, but not all applications. This is only an exemplary system. Design must be suited to fit the specific service.

TABLE 5-11. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH BASELINE HYDROGEN FLUORIDE STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
VESSELS:		
Storage Tank	131,000	15,000
PIPING AND VALVES:		
Pipework	2,300	270
Check Valve	280	30
Gate Valves (5)	1,700	200
Excess Flow Valves (2)	500	60
Angle Valves (2)	2,100	250
Relief Valve	2,000	240
PROCESS MACHINERY:		
Centrifugal Pump	4,000	460
INSTRUMENTATION:		
Pressure Gauges (4)	1,500	170
Liquid Level Gauge	1,500	170
PROCEDURES AND PRACTICES:		
Visual Tank Inspection (external)		15
Visual Tank Inspection (internal)		60
Relief Valve Inspection		15
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		30
Valve Maintenance		350
TOTAL COSTS	147,000	18,000

TABLE 5-12. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 1 HYDROGEN FLUORIDE STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
VESSELS:		
Storage Tank	187,000	22,000
Expansion Tanks (3)	6,500	760
PIPING AND VALVES:		
Pipework	6,200	720
Check Valve	560	65
Gate Valves (5)	1,700	200
Excess Flow Valves (2)	500	60
Angle Valves (2)	2,100	250
Relief Valves (2)	4,000	470
PROCESS MACHINERY:		
Centrifugal Pump	16,000	1,900
INSTRUMENTATION:		
Pressure Gauges (4)	1,500	175
Flow Indicator	3,700	430
Liquid Level Gauge	1,500	175
Remote Level Indicator	1,900	220
ENCLOSURES:		
Steel Building	10,000	1,200
SCRUBBERS:		
Water Scrubber	226,000	26,000

(Continued)

TABLE 5-12 (Continued)

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
DIKING:		
3 ft High Concrete Diking	1,400	160
PROCEDURES AND PRACTICES:		
Visual Tank Inspection (external)		15
Visual Tank Inspection (internal)		60
Relief Valve Inspection		30
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		35
Valve Maintenance		400
TOTAL COSTS	471,000	56,000

TABLE 5-13. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 2 HYDROGEN FLUORIDE STORAGE SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
VESSELS:		
Storage Tank	932,000	109,000
Expansion Tanks (3)	6,500	760
PIPING AND VALVES:		
Pipework	9,200	1,100
Reduced Pressure Device	1,500	170
Gate Valves (5)	1,700	200
Excess Flow Valves (2)	500	60
Angle Valves (2)	2,100	250
Relief Valves (2)	4,000	470
Rupture Disks (2)	1,100	130
PROCESS MACHINERY:		
Centrifugal Pump	19,000	2,200
INSTRUMENTATION:		
Temperature Indicator	2,200	260
Pressure Gauges (6)	2,200	260
Flow Indicator	3,700	430
Load Cell	16,000	1,900
Remote Level Indicator	1,900	220
Level Alarm	380	45
High-Low Level Shutoff	1,900	220
ENCLOSURES:		
Concrete Building	19,000	2,300

(Continued)

TABLE 5-13 (Continued)

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
SCRUBBERS:		
Alkaline Scrubber	280,000	33,000
DIKING:		
10 ft High Concrete Diking	7,600	500
PROCEDURES AND PRACTICES:		
External Tank Inspection		15
Internal Tank Inspection		60
Relief Valve Inspection		50
Piping Inspection		300
Piping Maintenance		120
Valve Inspection		35
Valve Maintenance		400
TOTAL COSTS	1,312,000	154,000

TABLE 5-14. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH BASELINE HYDROGEN FLUORIDE ALKYLATION REACTOR/SETTLER SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
EQUIPMENT:		
Vessels and Machinery:		
Reactor/Settler		
Feed Dryers (2)		
Centrifugal Pumps (3)		
Total Vessels and Machinery[a]	1,459,000	175,000
Piping and Valves:[a]	664,000	79,000
INSTRUMENTATION:[a]	302,000	36,000
Maintenance and Inspections:[a]		42,000
TOTAL COSTS	2,425,000	332,000

[a] Costs are based on using cost factors from Peters and Timmerhaus (48) and a total fixed capital cost of $10.06 million (1986 basis) (49) for a 147,000 gal/day alkylate capacity plant.

TABLE 5-15. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 1 HYDROGEN FLUORIDE ALKYLATION REACTOR/SETTLER SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
EQUIPMENT:		
Vessels and Machinery:		
Reactor/Settler		
Feed Dryers (2)		
Centrifugal Pumps (3)		
Total Vessels and Machinery[a]	2,646,000	318,000
Piping and Valves:[a]	943,000	114,000
Relief Valve	2,000	230
INSTRUMENTATION:[a]	302,000	36,000
Temperature Sensor	360	45
Temperature Alarm	360	45
Remote Temperature Indicator	1,800	220
Remote Pressure Indicator	1,800	220
Flow Control Loops (2)	11,000	1,300
Agitation Detection System and Alarm	1,800	220
DIKING:		
Curbing Around Reactor	1,200	150
SCRUBBER:		
Water Scrubber	260,000	31,000
MAINTENANCE AND INSPECTIONS:[a]		42,000
Relief Valve Inspection		15
TOTAL COSTS	4,172,000	544,000

[a] Costs are based on using cost factors from Peters and Timmerhaus (48) and a total fixed capital cost of $10.06 million (1986 basis) (49) for a 147,000 gal/day alkylate capacity plant.

TABLE 5-16. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH LEVEL 2 HYDROGEN FLUORIDE ALKYLATION REACTOR/SETTLER SYSTEM

	Capital Cost (1986 $)	Annual Cost (1986 $/yr)
EQUIPMENT:		
Vessels and Machinery:		
Reactor/Settler		
Feed Dryers (2)		
Centrifugal Pumps (3)		
Total Vessels and Machinery[a]	2,646,000	319,000
Piping and Valves:[a]	943,000	114,000
Relief Valves (2)	4,000	470
Rupture Disk	2,300	280
INSTRUMENTATION:[a]	302,000	36,000
Temperature Sensor	360	45
Temperature Alarm	360	45
Temperature Switch	540	65
Remote Temperature Indicator	1,800	220
Remote Pressure Indicator	1,800	220
Flow Control Loops (2)	11,000	1,300
Flow Interlock System	1,800	220
Agitation Detection System and Alarm	1,800	220
Mixing Interlock System	1,800	220
pH Monitoring System	9,000	1,100
Moisture Monitoring System	9,000	1,100
All Loops on Computer Control[b]	201,000	24,000
DIKING:		
3 ft High Retaining Wall	3,000	360
SCRUBBER:		
Alkaline Scrubber	312,000	38,000
MAINTENANCE AND INSPECTIONS:[a]		42,000
Relief Valve Inspection		25
TOTAL COSTS	4,453,000	579,000

[a] Costs are based on using cost factors from Peters and Timmerhaus (48) and a total fixed capital cost of $10.06 million (1986 basis) (49) for a 147,000 gal/day alkylate capacity plant.

[b] Computer Control costs are determined using cost estimating factors from Valle-Riestra (50).

5.8.4 Equipment Specifications and Detailed Costs

Equipment specifications and details of the capital cost estimates for the hydrogen fluoride storage and the hydrogen fluoride alkylation reactor systems are presented in Tables 5-17 through 5-24.

5.8.5 Methodology

Format for Presenting Cost Estimates--

Tables are provided for control schemes associated with storage and process facilities for hydrogen fluoride showing capital, operating, and total annual costs. The tables are broken down into subsections comprising vessels, piping and valves, process machinery, instrumentation, and procedures and practice. The presentation of the costs in this manner allows for easy comparison of costs for specific items, different levels, and different systems.

Capital Cost--All capital costs presented in this report are shown as total fixed capital costs. Table 5-25 defines the cost elements comprising total fixed capital as it is used here.

The computation of total fixed capital as shown in Table 5-25 begins with the total direct cost for the system under consideration. This total direct cost is the total direct installed cost of all capital equipment comprising the system. Depending on the specific equipment item involved, the direct capital cost was available or was derived from uninstalled equipment costs by computing costs of installation separately. To obtain the total fixed capital cost, other costs obtained by utilizing factors are added to the total direct costs.

The first group of other cost elements is indirect costs. These include engineering and supervision, construction expenses, and various other expenses such as administration expenses, for example. These costs are computed by multiplying total direct costs by a factor shown in Table 5-25. The factor is

TABLE 5-17. EQUIPMENT SPECIFICATIONS ASSOCIATED WITH HYDROGEN FLUORIDE STORAGE SYSTEM

Equipment Item	Equipment Specification	Reference
VESSELS:		
Storage Tank	Baseline: 10,000 gal. Carbon Steel Storage Tank, 150 psig Level #1: 10,000 gal. Carbon Steel With 1/8 in. Corrosion Protection, 225 psig Level #2: 10,000 gal. Monel® 375 psig	48,51,52 53
Expansion Tank	Standard Carbon Steel Pressure Vessel With Rupture Disk and Pressure Gauge	48,51
PIPING AND VALVES:		
Pipework	Baseline: 1 in. Schedule 80 Carbon Steel Level #1: 1 in. Schedule 80 Saran®-lined Carbon Steel Level #2: 1 in. Schedule 80 Monel®	54
Check Valve	1 in. Vertical Lift Check Valve, Monel® Trim	51,55
Gate Valve	1 in. Screwed, Monel® Trim, Bolted Bonnet	48,51,55
Excess Flow	1 in. Standard Valve	51
Angle Valves	1 in. Carbon Steel, Monel® Trim	56
Relief Valves	1 in. x 2 in., Class 300 Inlet and Outlet Flange, Angle Body, Closed Bonnet With Screwed Cap, Carbon Steel Body, Monel® Trim	51
Reduced Pressure Device	Double Check Valve Type Device With Internal Air Gap and Relief Valve	48
Rupture Disk	1 in. Monel® Disk and Carbon Steel Holder	52,57,58
PROCESS MACHINERY:		
Centrifugal Pump	Baseline: Single Stage, Carbon Steel Construction, Stuffing Box Level #1: Single Stage, Monel® Construction, Double Mech. Seal	51,59
	Level #2: Magnetically-coupled, Monel® Construction,	51,59

(Continued)

TABLE 5-17 (Continued)

Equipment Item	Equipment Specification	Reference
INSTRUMENTATION:		
Pressure Gauge	Diaphragm Sealed, Hastelloy C Diaphragm, 0-1,000 psi	48,51,54
Liquid Level Gauge	Differential Pressure Type	48,54
Temperature Indicator	Thermocouple, Thermowall, Electronic Indicator	48,51,54
Flow Indicator	Differential Pressure Cell and Transmitter and Associated Flowmeter	48,54
Level Indicator	Differential Pressure Type Indicator	48,51,54
Load Cell	Electrical Load Cell	48,54,60
Level Alarm	Indicating and Audible Alarm	51,56,61
High-low Level Shutoff	Solenoid Valve, Switch, and Relay System	48,51,54 56
ENCLOSURES:		
Building	Level #1: 26-Gauge Steel Walls and Roof, Door, Ventilation System Level #2: 10 in. Concrete Walls, 26-Gauge Steel Roof	56
SCRUBBERS:	Level #1: Spray Tower, Monel® Construction, Water Sprays, 6 ft. x 18 ft. Level #2: Spray Tower, Monel® Construction, Alkaline Sprays	62
DIKING:	Level #1: 6 in. Concrete Walls, 3 ft. High Level #2: 10 in. Concrete Walls, Top of Tank Height (10 ft.)	56

TABLE 5-18. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH BASELINE HYDROGEN FLUORIDE STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs (1986 $)	Indirect Costs	Capital Cost
VESSELS:					
Storage Tank	61,000	27,000	88,000	31,000	131,000
PIPING AND VALVES:					
Pipework	550	1,000	1,550	540	2,300
Check Valve	160	30	190	60	280
Gate Valves (5)	1,000	150	1,150	400	1,700
Excess Flow Valves (2)	300	40	340	120	500
Angle Valves (2)	1,400	40	1,440	500	2,100
Relief Valve	1,300	50	1,350	470	2,000
PROCESS MACHINERY:					
Centrifugal Pump	1,900	800	2,700	940	4,000
INSTRUMENTATION:					
Pressure Gauges (4)	800	200	1,000	350	1,500
Liquid Level Gauge	800	200	1,000	350	1,500
TOTAL COSTS	69,000	30,000	99,000	35,000	147,000

TABLE 5-19. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 1 HYDROGEN FLUORIDE STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
VESSELS:					
Storage Tank	87,000	39,000	126,000	44,000	187,000
Expansion Tanks (3)	3,500	880	4,380	1,500	6,500
PIPING AND VALVES:					
Pipework	3,300	860	4,160	1,500	6,200
Check Valves	320	60	380	130	560
Gate Valves (5)	1,000	150	1,150	400	1,700
Excess Flow Valves (2)	300	40	340	120	500
Angle Valves (2)	1,400	40	1,440	500	2,100
Relief Valves (2)	2,600	100	2,700	950	4,000
PROCESS MACHINERY:					
Centrifugal Pump	7,900	3,400	11,300	3,900	16,000
INSTRUMENTATION:					
Pressure Gauges (4)	800	200	1,000	350	1,500
Flow Indicator	2,000	500	2,500	880	3,700
Liquid Level Gauge	800	200	1,000	350	1,500
Remote Level Indicator	1,000	250	1,250	440	1,900
ENCLOSURES:					
Steel Building	4,600	2,300	6,900	2,400	10,000
SCRUBBERS:					
Water Scrubber	105,000	47,000	152,000	53,000	226,000

(Continued)

TABLE 5-19 (Continued)

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
DIKING:					
3 ft High Concrete Diking	390	520	910	320	1,400
TOTAL COSTS	222,000	95,000	317,000	111,000	471,000

TABLE 5-20. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 2 HYDROGEN FLUORIDE STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
VESSELS:					
Storage Tank	432,000	195,000	627,000	220,000	932,000
Expansion Tanks (3)	3,500	880	4,380	1,500	6,500
PIPING AND VALVES:					
Pipework	4,800	1,400	6,200	2,200	9,200
Reduced Pressure Device	800	200	1,000	350	1,500
Gate Valves (5)	1,000	150	1,150	400	1,700
Excess Flow Valves (2)	300	40	340	120	500
Angle Valves (2)	1,400	40	1,440	500	2,100
Relief Valves (2)	2,600	100	2,700	950	4,000
Rupture Disks (2)	650	80	730	260	1,100
PROCESS MACHINERY:					
Centrifugal Pump	9,000	3,900	12,900	4,500	19,000
INSTRUMENTATION:					
Temperature Indicator	1,200	300	1,500	530	2,220
Pressure Gauges (6)	1,200	300	1,500	530	2,200
Flow Indicator	2,000	500	2,500	880	3,700
Load Cell	8,400	2,100	10,500	3,700	16,000
Remote Level Indicator	1,000	250	1,250	440	1,900
Level Alarm	200	50	250	90	380
High-Low Level Shutoff	1,000	250	1,250	440	1,900
ENCLOSURES:					
Concrete Building	6,100	6,600	12,700	4,500	19,000

(Continued)

TABLE 5-20 (Continued)

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
SCRUBBERS:					
Alkaline Scrubber	130,000	59,000	189,000	66,000	280,000
DIKING:					
10 ft High Concrete Dike	2,200	2,900	5,100	1,800	7,600
TOTAL COSTS	609,000	274,000	884,000	310,000	1,312,000

TABLE 5-21. EQUIPMENT SPECIFICATIONS ASSOCIATED WITH HYDROGEN FLUORIDE ALKYLATION REACTOR/SETTLER

Equipment Item	Equipment Specification	Reference
VESSELS AND MACHINERY:		
Reactor/Settler	Gravity Flow Reactor/Settler System	49
Feed Dryers	Sieve Dryers or Equivalent on Reactor Feed Streams	49
PIPING AND VALVES:		
Relief Valve	2 in. x 3 in. Class 300 Inlet and Outlet Flange, Angle Body, Closed Bonnet With Screwed Cap, Carbon Steel Body, Monel® Trim	51
Rupture Disk	2 in. Monel® Disk and Carbon Steel Holder	52,57,58
INSTRUMENTATION:		
Temperature Sensor	Thermocouple and Associated Thermowell	48,51,54
Temperature Alarm	Indicating and Audible Alarm	51,56,61
Temperature Switch	Two-Stage Switch with Independently Set Actuation	48,54
Remote Temp. Indicator	Transmitter and Associated Electronics Indicator	48,54
Remote Press. Indicator	Transducer, Transmitter and Electronic Indicator	48,54
Flow Control Loop	2 in. Globe Control Valve, Monel® Trim, Flowmeter and PID Controller	48,54
Flow Interlock System	Solenoid Valve, Switch, and Relay System	48,51,54 56
Agitation Detection System and Alarm	Temperature Sensor Indicator and Alarm System for Phillips Reactor/Settler Design, Mechanical Agitation Detector for Others	48,54
Mixing Interlock System	Solenoid Valve, Switch, and Relay System	48,51,54 56
pH Monitoring System	Electrode, Electrode Chamber, Amplifier-Transducer and Indicator	48,60
Moisture Monitoring System	Capacitance or Infrared Absorption System	60

(Continued)

TABLE 5-21 (Continued)

Equipment Item	Equipment Specification	Reference
DIKING:	Level #1: 6 in. High Concrete Curbing Level #2: 3 ft High Concrete Retaining	56
SCRUBBER:	Level #1 Spray Tower, Monel® Construction, Water Sprays, 8 ft. x 24 ft. Level #2 Spray Tower, Monel® Construction, Alkaline Sprays	62

TABLE 5-22. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH BASELINE HYDROGEN FLUORIDE ALKYLATION REACTOR/SETTLER SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
EQUIPMENT:					
Vessels and Machinery:					
Reactor/Settler					
Feed Dryers (2)					
Centrifugal Pumps (3)					
Total Vessels and Machinery[a]	700,000	315,000	1,015,000	254,000	1,459,000
Piping and Valves:[a]	252,000	210,000	462,000	115,000	664,000
INSTRUMENTATION:[a]	158,000	52,000	210,000	52,000	302,000
TOTAL COSTS	1,110,000	577,000	1,687,000	421,000	2,425,000

[a] Costs are based on using cost factors from Peters and Timmerhaus (48) and a total fixed capital cost of $10.06 million (1986 basis) (49) for a 147,000 gal/day alkylate capacity plant.

TABLE 5-23. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 1 HYDROGEN FLUORIDE ALKYLATION REACTOR/SETTLER SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
EQUIPMENT:					
Vessels and Machinery:					
Reactor/Settler					
Feed Dryers (2)					
Centrifugal Pumps (3)					
Total Vessels and Machinery[a]	1,270,000	571,000	1,841,000	460,000	2,646,000
Piping and Valves:[a]	492,000	164,000	656,000	164,000	943,000
Relief Valve	1,300	50	1,350	340	2,000
INSTRUMENTATION:[a]	158,000	52,000	210,000	52,000	302,000
Temperature Sensor	200	50	250	60	360
Temperature Alarm	200	50	250	60	360
Remote Temperature Indicator	1,000	250	1,250	310	1,800
Remote Pressure Indicator	1,000	250	1,250	310	1,800
Flow Control Loops (2)	6,000	1,500	7,500	1,900	11,000
Agitation Detection System and Alarm	1,000	250	1,250	310	1,800
DIKING:					
Curbing Around Reactor	500	350	850	210	1,200
SCRUBBER:					
Water Scrubber	125,000	56,000	181,000	45,000	260,000
TOTAL COSTS	2,056,000	846,000	2,902,000	725,000	4,172,000

[a] Costs are based on using cost factors from Peters and Timmerhaus (48) and a total fixed capital cost of $10.06 million (1986 basis) (49) for a 147,000 gal/day alkylate capacity plant.

TABLE 5-24. DETAILS OF MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 2 HYDROGEN FLUORIDE ALKYLATION REACTOR/SETTLER SYSTEM

	Materials Cost	Labor Cost	Direct Costs	Indirect Costs	Capital Cost
			(1986 $)		
EQUIPMENT:					
Vessels and Machinery:					
Reactor/Settler					
Feed Dryers (2)					
Centrifugal Pumps (3)					
Total Vessels and Machinery[a]	1,270,000	571,000	1,841,000	460,000	2,646,000
Piping and Valves:[a]	492,000	164,000	656,000	164,000	943,000
Relief Valves (2)	2,600	100	2,700	680	4,000
Rupture Disk	1,500	100	1,600	400	2,300
INSTRUMENTATION:[a]	158,000	52,000	210,000	52,000	301,000
Temperature Sensor	200	50	250	60	360
Temperature Alarm	200	50	250	60	360
Temperature Switch	300	75	375	95	540
Remote Temperature Indicator	1,000	250	1,250	310	1,800
Remote Pressure Indicator	1,000	250	1,250	310	1,800
Flow Control Loops (2)	6,000	1,500	7,500	1,900	11,000
Flow Interlock System	1,000	250	1,250	310	1,800
Agitation Detection System and Alarm	1,000	250	1,250	310	1,800
Mixing Interlock System	1,000	250	1,250	310	1,800
pH Monitoring System	5,000	1,300	6,300	1,600	9,000

(Continued)

TABLE 5-24 (Continued)

	Materials Cost	Labor Cost	Direct Costs (1986 $)	Indirect Costs	Capital Cost
Moisture Monitoring System	5,000	1,300	6,300	1,600	9,000
All Loops on Computer Control[b]	105,000	35,000	140,000	35,000	201,000
DIKING:					
Retaining Wall	900	1,200	2,100	530	3,000
SCRUBBER:					
Alkaline Scrubber	150,000	67,000	217,000	54,000	312,000
TOTAL COSTS	2,202,000	896,000	3,098,000	775,000	4,453,000

[a] Costs are based on using cost factors from Peters and Timmerhaus (48) and a total fixed capital cost of $10.06 million (1986 basis) (49) for a 147,000 gal/day alkylate capacity plant.

[b] Computer Control costs are determined using cost estimating factors from Valle-Riestra (50).

TABLE 5-25. FORMAT FOR TOTAL FIXED CAPITAL COST

Item No.	Item	Cost
1	Total Material Cost	–
2	Total Labor Cost	–
3	Total Direct Cost	Items 1 + 2
4	Indirect Cost Items (Engineering & Construction Expenses)	0.35 x Item 3[a]
5	Total Bare Module Cost	Items (3 + 4)
6	Contingency	(0.05 x Item 5)[b]
7	Contractor's Fee	0.05 x Item 5
8	Total Fixed Capital Cost	Items (5 + 6 + 7)

[a] For storage facilities, the indirect cost factor is 0.35. For process facilities, the indirect cost factor is 0.25.

[b] For storage facilities, the contingency cost factor is 0.05. For process facilities, the contingency cost factor is 0.10.

approximate, is obtained from the cost literature, and is based on previous experience with capital projects of a similar nature. Factors can have a range of values and vary according to technology area and for individual technologies within an area. Appropriate factors were selected for use in this report based on judgement and experience.

When the indirect costs are added to the total direct costs, total bare module cost is obtained. Some additional cost elements such as contractor's fee and contingency are calculated by applying and adding appropriate factors to the total bare module cost as shown in Table 5-25 to obtain the total fixed capital cost.

Annual Cost--Annual costs are obtained for each of the equipment items by applying a factor for both capital recovery and for maintenance expenses to the direct cost of each equipment item. Table 5-26 defines the cost elements and appropriate factors comprising these costs. Additional annual costs are incurred for procedural items such as valve and vessel inspections, for example. When all of these individual costs are added, the total annual cost is obtained.

Sources of Information--

The costs presented in this report are derived from cost information in existing published sources and also from recent vendor information. It was the objective of this effort to present cost levels for hydrogen fluoride process and storage facilities using the best costs for available sources. The primary sources of cost information are Peters and Timmerhaus (48), Chemical Engineering (63), and Valle-Riestra (49) supplemented by other sources and references where necessary. Adjustments were made to update all costs to a June 1986 dollar basis. In addition, for some equipment items, well-documented costs were not available and they had to be developed from component costs.

TABLE 5-26. FORMAT FOR TOTAL ANNUAL COST

Item No.	Item	Cost
1	Total Direct Cost	-
2	Capital Recovery on Equipment Items	0.163 x Item 1
3	Maintenance Expense on Equipment Items	0.01 x Item 1
4	Total Procedural Items	-
5	Total Annual Cost	Items (2 + 3 + 4)

*Based on a capital recovery factor at 10% cost of capital for 10 years.

Costs in this document reflect the "typical" or "average" representation for specific equipment items. This restricts the use of data in this report to:

- Preliminary estimates used for policy planning,
- Comparison of relative costs of different levels or systems, and
- Approximations of costs that might be incurred for a specific application.

The costs in this report are considered to be "order of magnitude" with a ±50 percent margin. This is because the costs are based on preliminary estimates and many are updated from literature sources. Large departures from the design basis of a particular system presented in this manual or the advent of a different technology might cause the system cost to vary by a greater extent than this. If used as intended, however, this document will provide a reasonable source of preliminary cost information for the facilities covered.

When comparing costs in this manual to costs from other references, the user should be sure the design bases are comparable and that the capital and annual costs as defined here are the same as the costs being compared.

Cost Updating--

All costs in this report are expressed in June 1986 dollars. Costs reported in the literature were updated using cost indices for materials and labor.

Costs expressed in base year dollars may be adjusted to dollars for another year by applying cost indices as shown in the following equation:

$$\text{new base year cost} = \text{old base year cost} \times \frac{\text{new base year index}}{\text{old base year index}}$$

The Chemical Engineering (CE) Plant Cost Index was used in updating cost for this report. For June 1986, the index is 316.3.

Equipment Costs--

Most of the equipment costs presented in this manual were obtained directly from literature sources of vendor information and correspond to a specific design standard. Special cost estimating techniques, however, were used in determining the costs associated with vessels, piping systems, scrubbers, diking, and enclosures. The techniques used are presented in the following subsections of this manual.

Vessels--The total purchased cost for a vessel, as dollars per pound of weight of fabricated unit free on board (f.o.b.) with carbon steel as the basis (January 1979 dollars) were determined using the following equation from Peters and Timmerhaus (48):

$$\text{Cost} = [50(\text{Weight of Vessel in Pounds})^{-0.34}]$$

The vessel weight is determined using appropriate design equations as given by Peters and Timmerhaus (48) which allow for wall thickness adjustments for corrosion allowances, for example. The vessel weight is increased by a factor of 0.15 for horizontal vessels and 0.20 for vertical vessels to account for the added weight due to nozzles, manholes, and skirts or saddles. Appropriate factors are applied for different materials of construction as given in Peters and Timmerhaus (48). The vessel costs are updated using cost factors. Finally a shipping cost amounting to 10 percent of the purchased cost is added to obtain the delivered equipment cost.

Piping--Piping costs were obtained using cost information and data presented by Yamartino (64). A simplified approach is used in which it is assumed that a certain length of piping containing a given number of valves, flanges, and fittings is contained in the storage or process facility. the data presented by Yamartino (64) permit cost determinations for various lengths, sizes, and types of piping systems. Using these factors, a representative estimate can be obtained for each of the storage and process facilities.

Diking--Diking costs were estimated using Mean's Manual (56) for reinforced concrete walls. The following assumptions were made in determining the costs. The dike contains the entire contents of a tank in the event of a leak or release. Two dike sizes are possible: a three-foot high dike, six-inches thick and a top-of-tank height dike ten inches thick. The tanks are raised off the ground and are not volumetrically included in the volume enclosed by the diking. These assumptions facilitate cost determination for any size diking system.

Enclosures--Enclosure costs were estimated using Mean's Manual (56) for both reinforced concrete and steel-walled buildings. The buildings are assumed to enclose the same area and volume as the top-of-tank height dikes. The concrete building is ten-inches thick with a 26-gauge steel roof and a metal door. The steel building has 26 gauge roofing and siding and metal door. The cost of a ventilation system was determined using a typical 1,000 scfm unit and doubling the cost to account for duct work and requirements for the safe enclosure of hazardous chemicals.

Scrubbers--Scrubber costs were estimated using the following equation from the Gard (62) manual for spray towers based on the actual cubic feet per minute of flow at a chamber velocity of 600 feet/minute.

$$\text{Costs} = 0.235 \times (\text{ACFM} + 43{,}000)$$

A release rate of 10,000 ft^3/minute was assumed for the storage vessel systems and an appropriate rate was determined for process system based on the quantity of hazardous chemicals present in the system at any one time. For the hydrogen fluoride alkylation system, a release rate of 36,000 ft^3/minute was assumed. In addition to the spray tower, the costs also include pumps and a storage tank for the scrubbing medium. The costs presented are updated to June 1986 dollars.

Installation Factors--

Installation costs were developed for all equipment items included in both the process and storage systems. The costs include both the material and labor costs for installation of a particular piece of equipment. The costs were obtained directly from literature sources and vendor information or indirectly by assuming a certain percentage of the purchased equipment cost through the use of estimating factors obtained from Peters and Timmerhaus (48) and Valle-Riestra (50). Table 5-27 lists the cost factors used or the reference from which the cost was obtained directly. Many of the costs obtained from the literature were updated to June 1986 dollars using a 10 percent per year rate of increase for labor and cost indices for materials associated with installation.

TABLE 5-27. FORMAT FOR INSTALLATION COSTS

Equipment Item	Factor or Reference
Vessels:	
Storage Tank	0.45
Expansion Tank	0.25
Piping and Valves:	
Pipework	Ref. 64
Expansion Loop	Ref. 51
Reduced Pressure Device	Ref. 51
Check Valves	Ref. 51
Gate Valves	Ref. 51
Ball Valves	Ref. 51
Excess Flow Valves	Ref. 51
Angle Valves	Ref. 56
Relief Valves	Ref. 51
Rupture Disks	Ref. 51
Process Machinery:	
Centrifugal Pump	0.43
Gear Pump	0.43
Instrumentation:	
All Instrumentation Items	0.25
Enclosures:	Ref. 56
Diking:	Ref. 56
Scrubbers:	0.45

SECTION 6

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APPENDIX A

ELECTROMOTIVE SERIES OF METALS

TABLE A-1. ELECTROMOTIVE SERIES OF METALS

Least noble

Lithium
Potassium
Rubidium
Calcium
Sodium
Magnesium
Plutonium
Beryllium
Uranium
Aluminum
Titanium
Zirconium
Manganese
Tantalum
Zinc
Chromium
Iron
Cadmium
Nickel
Molybdenum
Tin
Lead
Tungsten
HYDROGEN
copper
Mercury
Silver
Gold
Platinum
Palladium

Most noble

Source: Reference 65

APPENDIX B

GLOSSARY

This glossary defines selected terms used in the text of this manual which might be unfamiliar to some users or which might be used differently by different authors.

Accidental release: The unintentional spilling, leaking, pumping, purging, emitting, emptying, discharging, escaping, dumping, or disposing of a toxic material into the environment in a manner that is not in compliance with a plant's federal, state, or local environmental permits and that creates toxic concentrations in the air that are a potential health threat to the surrounding community.

Cavitation: The formation and collapse of vapor bubbles in a flowing liquid. Specifically, the formation and collapse of vapor cavities in a pump or compressor when there is sufficient resistance to flow at the inlet side.

Chlorofluorocarbons: Organic compounds containing chlorine and/or fluorine atoms within the molecule.

Creep failure: Failure of a piece of metal as a result of creep. Creep is time dependent deformation as a result of stress. Metals will deform when exposed to stress. High levels of stress can result in rapid deformation and rapid failure. Lower levels of stress can result in slow deformation and protracted failure.

Deadheading: Closing or nearly closing or blocking the discharge outlet or piping of an operating pump or compressor.

Electromotive Series of Metals: A list of metals and alloys arranged according to their standard electrode potential which also reflects their relative corrosion potential.

Enthalpy: A thermodynamic property of a chemical related to its energy content at a given condition of temperature, pressure, and physical state. Enthalpy is the internal energy added to the product of pressure times volume. Numerical values of enthalpy for various chemicals are always based on the change in enthalpy from an arbitrary reference pressure, temperature and physical state, since the absolute value cannot be measured.

Facility: A location at which a process or set of processes are used to produce, refine or repackage chemicals, or a location where a large enough inventory of chemicals are stored so that a significant accidental release of a toxic chemical is possible.

Hazard: A source of danger. The potential for death, injury or other forms of damage to life and property.

Hygroscopic: Readily absorbing and retaining moisture, usually in reference to readily absorbing moisture from the air.

Killed steel: Steel that is deoxidized with a strong deoxidizing agent such a silicon or aluminum in order to reduce the oxygen content to such a level that no reaction occurs between carbon and oxygen during solidification. Such a steel will have a smaller grain size than a steel that is not killed. The grain size affects the physical and chemical properties of the steel. Fully-killed steel is fully deoxidized and has a smaller grain size than semi-killed steel which is partially deoxidized and has a smaller grain size than steel that is not killed.

Mild steel: Carbon steel containing a maximum of about 0.25% carbon. Mild steel is satisfactory for use where severe corrodants are not encountered or where protective coatings can be used to prevent or reduce corrosion rates to acceptable levels.

Mitigation: Any measure taken to reduce the severity of the adverse effects associated with the accidental release of a hazardous chemical.

Olefinic hydrocarbons: A specific subgroup of aliphatic hydrocarbons sharing the common characteristic of at least one unsaturated carbon-to-carbon atomic bond in the hydrocarbon molecule. Aliphatic hydrocarbons are hydrocarbons with a basic straight or branched chain structure in contrast with ring structured compounds.

Passivation film: A layer of oxide or other chemical compound of a metal on its surface that acts as a protective barrier against corrosion or further chemical reaction.

Plant: A location at which a process or set of processes are used to produce, refine or repackage chemicals.

Prevention: Design and operating measures applied to a process to ensure that primary containment of toxic chemicals is maintained. Primary containment means confinement of toxic chemicals within the equipment intended for normal operating conditions.

Process: The sequence of physical and chemical states and operations for the production, refining, or repackaging of chemicals.

Process machinery: Process equipment such as pumps, compressors, or agitators that would not be categorized as piping and vessels.

Protection: Measures taken to capture or destroy a toxic chemical that has breached primary containment, but before an uncontrolled release to the environment has occurred.

Toxicity: A measure of the adverse health effects of exposure to a chemical.

APPENDIX C

TABLE C-1. METRIC (SI) CONVERSION FACTORS

Quantity	To Convert From	To	Multiply By
Length:	in	cm	2.54
	ft	m	0.3048
Area:	in^2	cm^2	6.4516
	ft^2	m^2	0.0929
Volume:	in^3	cm^3	16.39
	ft^3	m^3	0.0283
	gal	m^3	0.0038
Mass (weight):	lb	kg	0.4536
	short ton (ton)	Mg	0.9072
	short ton (ton)	metric ton (t)	0.9072
Pressure:	atm	kPa	101.3
	mm Hg	kPa	0.133
	psia	kPa	6.895
	psig	kPa*	(psig+14.696)x(6.895)
Temperature:	°F	°C*	(5/9)x(°F-32)
	°C	K*	°C+273.15
Caloric Value;	Btu/lb	kJ/kg	2.326
Enthalpy:	Btu/lbmol	kJ/kgmol	2.326
	kcal/gmol	kJ/kgmol	4.184
Specific-Heat Capacity:	Btu/lb-°F	kJ/kg-°C	4.1868
Density:	lb/ft^3	kg/m^3	16.02
	lb/gal	kg/m^3	119.8
Concentration:	oz/gal	kg/m^3	7.490
	quarts/gal	cm^3/m^3	25,000
Flowrate:	gal/min	m^3/min	0.0038
	gal/day	m^3/day	0.0038
	ft^3/min	m^3/min	0.0283
Velocity:	ft/min	m/min	0.3048
	ft/sec	m/sec	0.3048
Viscosity:	centipoise (CP)	kg/m-s	0.001

*Calculate as indicated